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VOLUME XIII AUGUST 25, 1924 NUMBER 14

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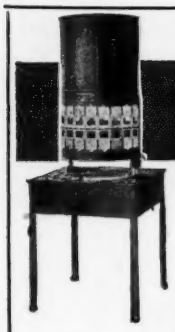

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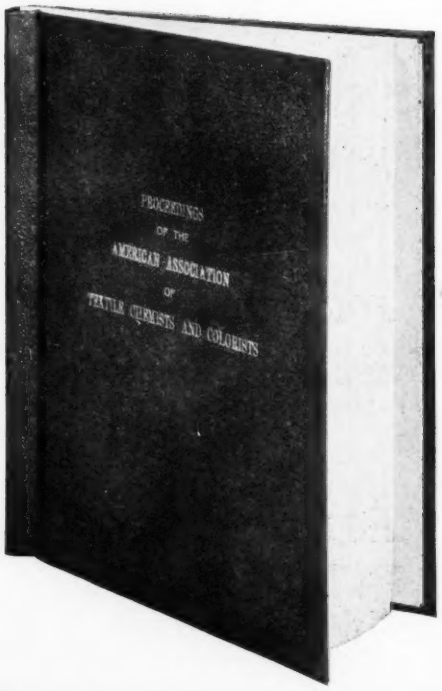

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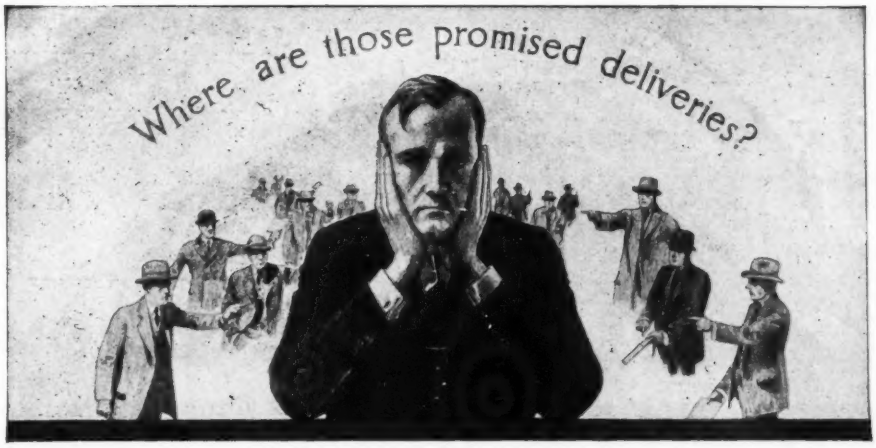

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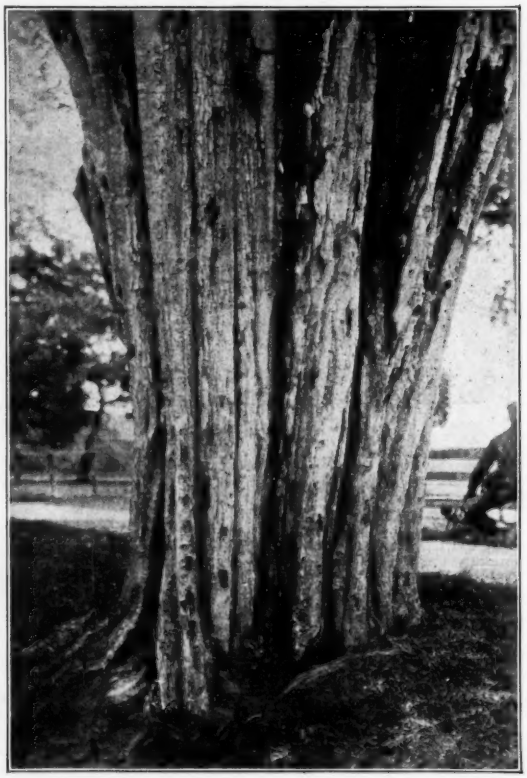

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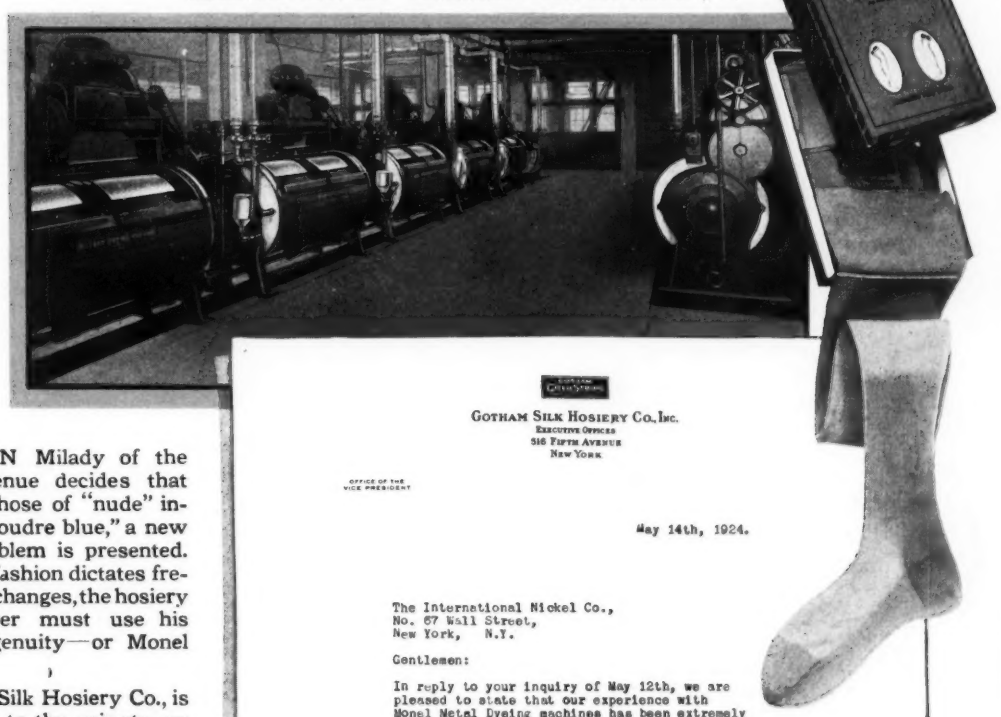

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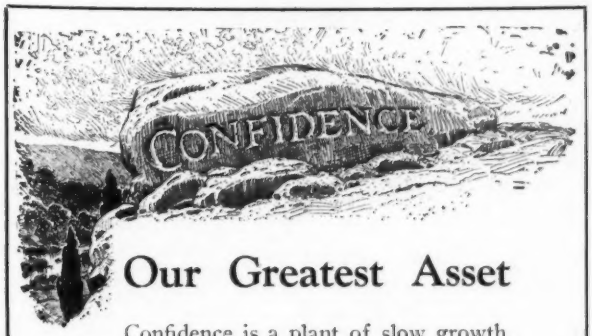

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VOLUME XIII NEW YORK, AUGUST 25, 1924 NUMBER 14

Application of Colloidal Chemistry to Textile Problems

Close Relationship Between Chemistry and Physics—Colloidal Solutions Known to Alchemists—Extensive Application of Colloidal Chemistry Recently Recognized—Emulsions Dispersions of Liquids—Formation of Emulsifying Agents—Dispersions of Solids—Relation of Movement to Dye Adsorption—Action of Emulsifying Agents—Adsorption of Solids by Solids

By ALAN A. CLAFLIN

THERE is a story told of an old sea captain who strayed one day into a fashionable restaurant and, to his annoyance, found the menu was in French. His reading acquaintance with this language being slight, he selected something near the top, and moderate in price, and ordered *bouillon*. His comment on finishing his portion was that he had sailed upon it all his life but did not know what its name was before.

Many engaged in various branches of the textile industry, from scouring the raw fibers to dyeing and finishing the ultimate product, will have an attitude of mind not unlike the sea captain if they look into the subject of colloidal chemistry. They have had to do with it all their lives but have not known its name. In some ways the name "colloid" is unfortunate, as its derivation from the Greek word for glue implies a narrower limitation or closer confine to this branch of science than is to-day true.

To sketch the development of colloidal chemistry and to show how the chemical problems of the textile industry are problems of the chemistry of colloids is the purpose of this paper. While certain examples of what is now known as colloidal chemistry can be traced back to the alchemists, the history of the science truly begins with the publicity of the work of the English chemist Thomas Graham from 1861 to 1864. Rightly is Graham recognized as the father of that branch of chemical science which treats of the behavior of the substances he distinguished as colloids, and which is becoming more and more identified as the chemistry of material things. Further, to him we are indebted for terms and nomenclature as well as for the enunciation of first principles in this ever-expanding division of science.

Close Relationship Between Chemistry and Physics

It should be emphasized at the outset that the chemistry of colloids is not of itself a distinctive variety or sub-division of chemistry. It has to do with the same chemical principles, the same elements, the same forces that are characteristic of all chemistry. Nowadays it is rather hazardous to lay down dividing lines between physics and chemistry, because the sciences are so intermingled that one does not know exactly where one begins and the other leaves off. The new science of the arrangement of nuclei and electrons, which constitute a chemical atom, is, under the name "atomistics," considered a department of physics. The behavior of the atoms themselves and their combination into ions and molecules is chemistry. When, however, the molecules are grouped into colloidal particles or micellae one has colloidal chemistry part physics and part chemistry. Thus the question of physics or chemistry becomes a question of aggregation or mass.

Dialysis the Test

Graham in his researches observed that substances of crystalline nature in solution can pass through certain semi-permeable membranes, while substances of a gummy character cannot. To the former he gave the name "crystalloids," to the latter the name "colloids." In his experiments Graham used as a semi-permeable membrane a parchmentized paper, and the method of separation by this means of crystalloids from colloids he termed "dialysis." He distinguished the true solution of the crystal-

loids from the apparent solution of the colloids and termed the colloidal solution "sols," while the jelly formed when the sols are cooled, concentrated or otherwise coagulated he termed "gels." He made the assumption, which has since been abundantly proved experimentally, that the essential distinction between a true solution and a sol is the size or state of aggregation of the colloidal particles in the sol.

Colloidal Solutions Known to Alchemists

Previous to Graham's time—indeed to the alchemists—had been known apparent solutions of certain metals, and these, he observed, had similar properties to the sols obtained from gummy substances. Thus we may define a sol as a system in which a substance in a solid phase is dispersed in another substance in a liquid phase. Extending this definition, for the same principles are found to apply, colloidal chemistry is the study of the chemical behavior of substances in system of two or more phases. By the phase of substances is meant their state as gases, liquids or solids. To make our definition more specific, we may quote Professor Bancroft, one of the leading American investigators and elucidators of colloidal phenomena: "Colloidal chemistry is the chemistry of bubbles, drops, grains, filaments and fibers." To quote the same authority further: "At first sight colloid chemistry may not seem to be an important branch of chemistry, either theoretically or technically; but this opinion changes when we consider that a knowledge of colloid chemistry is essential to anybody who really wishes to understand about cement, bricks, pottery, porcelain, glass, enamels; oils, greases, soaps, candles; glue, starch and adhesives; paints, varnishes, lacquers; rubber, celluloid and other plastics; leather, paper, textiles; filaments, casts, pencils and crayons; inks; roads, foundry cores, coke, asphalt; graphites, patines; zinc, phosphorus, sodium and aluminum; contact sulphuric acid, hardened oils, etc.; beer, ale and wine; cream, butter, cheese and casein products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal; smoke prevention; photography; wireless telegraphy; illuminants; comets; pharmacy; physiology. In other words, colloid chemistry is the chemistry of everyday life."

The importance of colloid chemistry to the textile chemist needs no more amplification.

Extensive Application of Colloidal Chemistry Recently Recognized

It is, however, only recently that it has been recognized that the principles underlying colloid chemistry had this extensive application. Indeed, only sixty years have elapsed since the publication of Graham's researches, and for four decades their importance was largely unappreciated; so the newness of this branch of chemical science must be emphasized. On the other hand, since colloid chemistry is the chemistry of everyday material operations, the arts with which colloid chemistry has to do are in the main very ancient. There is thus great danger, in considering these arts from the standpoint of colloid chemistry, that there will be no real contribution to the arts but a mere restatement of old problems in different language.

Gain from New Point of View

Too much must not be expected of the new chemistry at the outset, but the contribution of a new viewpoint or a new method of attack on old problems is usually productive of ultimate gain. Thus the discovery of the X-ray seems far removed from or to have little connection with the constitution of the chemical atom, yet this atom, which had resisted all methods of chemistry, yielded to the investigations of the physicists by experiments and deductions predicated on X-ray phenomena. Astronomy and the bothersome fractions in atomic weights seem as remote from each other as can conceivably be imagined, yet celestrial chemistry, the study of the spectra of the stars, was a fundamental factor in the discovery or proof of the existence of iso-topes.

The study of sols, those apparent solutions that will not dialyze, does not seem promising as a means of determining why one dyestuff is fast and another is not, nor why dyestuffs have less affinity for cotton than for wool; but when it is appreciated that these latter are only more complex problems of the same branch of chemistry, the study of the simpler example seems worth while.

Adsorption of Gases

The war gave great incentive to the study of the adsorption of gases by various charcoals. This is a study of colloid chemistry, a two-phase system, one a gaseous and the other a solid; or in many instances a three-phase system, with the "poisonous gas" really a highly dispersed liquid in the true gas, air, from which it is adsorbed by the surface of the charcoal. Dyeing is a problem of adsorption by the fiber surfaces. According to conditions, the dyestuff may be in true solution or a sol.

Emulsions Dispersions of Liquids

Emulsions are dispersions of fine drops of a liquid in another liquid in which it is insoluble. The particular emulsions with which the textile industry has most to do are that of oil in water and water in oil.

It should be pointed out that there is a distinction

between an oil-in-water emulsion and a water-in-oil emulsion. This distinction is independent of which is quantitatively the preponderant constituent; and while in the more familiar examples the dispersion medium is usually greatly in excess of the dispersed, this is by no means necessarily the case. Emulsions as such are used as lubricants for textile fibers, as well as frequently for machinery itself. It is perhaps not generally appreciated that the majority of lubricating greases are emulsions of water in oil. For cleansing textile fibers, detergents are used which are emulsifying agents, and the nature and action of these may be considered in the light of colloidal chemical theory. Emulsions may be extremely temporary or permanent and all degrees between, but for practical purposes the permanent or nearly permanent emulsions are the only ones of interest to discuss.

Formation of Emulsions

It is ordinary observation that when two immiscible liquids are stirred together they separate into two layers as soon as the stirring ceases. This separation into layers is caused by the small drops formed by the agitation coalescing into larger drops, and the larger drops into still larger ones until each liquid is by itself. To prepare an emulsion it is necessary to have agitation to break the dispersed liquid into fine drops and an emulsifying agent. The function of the emulsifying agent is to prevent the fine drops from coalescing. The action of the emulsifying agent is due to its adsorption on the surface of the fine drops, and the formation of an emulsion is as truly a phenomenon of adsorption as is the removal of toxic fumes by the charcoal of a gas mask. The surface of the fine drops in which the emulsifying agent is adsorbed is termed the interfacial surface; particles of colloidal size are for certain special reasons particularly prone to be adsorbed on this interfacial surface.

Varieties of Emulsifying Agents

Gums are for some purposes useful as emulsifying agents—e. g., in the popular emulsion of the pharmacy—but are vastly less efficient than the soaps. It should be noted that to emulsify oil in water, a water-soluble soap is used; to make a water-in-oil emulsion an insoluble soap is used. Oils which have had their viscosity increased by treatment with sulphuric acid are useful emulsifying agents, and their industrial applications based on this property are being extended all the time. In many instances, while sufficiently finely divided to be in the colloidal state, they act as emulsifying agents. It is probable that the emulsified condition that makes the separation of oil so difficult from the condensed exhaust steam from steam engines is due to finely divided metal or carbon.

The heavy greases so much used for lubrications are usually emulsions of water in a heavy mineral oil with a magnesium, calcium or aluminum soap acting as an emulsifying agent. The mineral oil, which in this case is the dispersion medium, is forced together and solidified by the pressure of the dispersed globules of water, which are kept from coalescing by insoluble soap in their interfacial surface.

Lubricants for wool carding formerly were rancid oils in which the free fatty acid acted as an emulsifying agent, but now sulphonated oils have largely replaced these naturally "turned" oils.

With the grease naturally occurring in the wool on the sheep's back are associated cholestrol and analogous bodies that are emulsifying agents, and these make the separating of this grease from the wash waters in scouring operations such a difficult problem.

Cotton softeners are emulsions of oil in water with various soaps used as emulsifying agents. The relatively less soluble soaps of stearic acid are widely used for this purpose. It has been claimed that the amide formed by heating the ammonia soap of stearic acid under pressure is particularly efficient for emulsions for cotton softeners, but to what extent this has been actually used in practice is a debatable question. In American practice certainly the ammonia soap has been used much more than the amide. Tallow is usually the fat that is dispersed. It has been suggested that for purposes of cotton softening a more effective softener would be obtained by using one of the insoluble soaps and having the emulsion one of water in oil; whether this has been tried out practically is doubtful.

Dispersions of Solids

In many ways the behavior of colloidal solutions in which the substance in the dispersed phase is a solid offers the simplest examples for studying the principles involved. It is fundamentally essential that the solids are in a state of extreme subdivision. As has already been pointed out, the metallic sols are the oldest known examples of artificial colloidal solutions, gold and silver sols having been known to the alchemists. Gold sols are readily prepared by reducing a very dilute alkaline gold chloride, and such sols are relatively permanent. While these sols have the appearance of true solutions, Faraday proved that the metal was present in suspension in an extremely finely divided state by passing a beam of light through the sol. While the particles, having dimensions less than the wave length of light, cannot be seen as particles, yet they will have the effect of scattering or polarizing the light and be visible as luminous points. Tyndall subsequently applied this method to the examination of air and gases, and the use of a strong beam of light to prove the presence of particles smaller than magnifiable visibity is known as the Tyndall effect. Rela-

tively recently an extension of the Tyndall effect has been developed by Zsigmondy with what is known as the ultra-microscope. The ultra-microscope is an ordinary microscope arranged so that its magnifying power is directed toward a beam of light passing through the liquid to be examined, all other illumination being excluded. The development of the ultra-microscope has been of great assistance in the experimental side of colloid chemistry. By its use the heterogeneity of sols has been irrefutably established, and, further, it has made it possible to establish the size of the particles.

Movement of Suspended Particles

It is common observation that the more finely divided a solid is the longer it will stay in suspension—either in air, as in a dust cloud, or as the slow settling muddy waters; and it is an obvious inference that if a solid is sufficiently finely divided it will not settle at all. That this is true, irrespective of the specific gravity of the particles, is proved by the gold sols, in which one of the heaviest of metals is in a state of suspension, because it is in such extreme subdivision. As long ago as 1828 James Brown, an English botanist, observed that fine particles of pollen suspended in water were in constant motion. That this motion was not due to thermal conditions or convection currents in the liquid was proved by careful insulation. When metallic sols were illuminated by the Faraday-Tyndall light cone and the same movements noted, it was further appreciated that the movements were the more violent the smaller the particles. Finally, with the aid of the ultra-microscope and photographic apparatus, it was definitely established, as had been earlier predicted, that this Brownian movement, named from its discoverer, is caused by the impact or bombardment of the particles by the molecules of the liquid in which they are suspended. The size of the particles known the study of their motion has contributed to our knowledge of the size and rapidity of motion of the molecules themselves.

Relation of Movement to Dye Adsorption

Now, having established that the motion of colloidal particles is due to the impact of molecules, it is a readily conceivable inference that the adsorption of a *dye* by a fiber is also due to this molecular impact. Thus, in a state of free suspension the particles are subjected to bombardment from all sides; but as they approach a surface in which molecular motion is more rigidly confined the number of impacts from the liquid will be greater than from the surface, and the effect may be that the particles are plastered onto the fiber by the impact of the molecules. In all probability the phenomenon of adsorption is not quite so simple as would appear from this statement, for in the first place the nature of the impact is not, as might be inferred, a direct physical impact, as of marbles against a baseball, but similar to the repulsion of a pith ball by an opposite electric charge as shown in the familiar elementary electricity experiment. Also, the electric charges of the colloidal particles themselves are to be considered and the electric charges of the fibers, both of which have in part to do with the chemical composition or chemical affinities as was the old-fashioned indefinite generalization.

Action of Emulsifying Agents

For simplicity's sake, if we adhere to the supposition of simple plastering, it is easy to understand the action of finely divided solids as emulsifying agents. The suspended particles are plastered against the surface of the dispersed globules as a protective coating, and these coatings prevent the globules from coalescing. If the proportion of non-coalescing globules is large in proportion to the dispersion medium, we have the formation of a gel. Gels are usually formed by cooling, by the addition of coagulants, or by the extruction of water or whatever the dispersion medium happens to be. Particularly with gels formed by the extruction of water, it is easy to infer that the gel is constituted of globules in surface contact, but not merging entirely into one another and with the remnant of the dispersion media filling interstitial space. That such is the case can be proved experimentally by diffusion experiments. In fact, for many purposes gels make very desirable semi-permeable membranes. In the examination of dyestuffs sufficient attention is not usually given to the possibility of identifying mixtures of dyes by the difference in diffusibility through gels; e. g., those of agar-agar are particularly suited for this purpose.

Adsorption of Solids by Solids

The final system in colloid chemistry to consider—that of a system of heterogeneous solids—comprises the most complex phenomena. Practically speaking, in such a system there is always a third component; viz., the gaseous phase that is adsorbed by the solids under consideration.

Inasmuch as adsorption is a surface phenomenon, the less the surface—in other words, the smoother the surface—the smaller the quantity of adsorbed air. Thus, very highly polished metal disks superimposed on one another will adhere together and require considerable force to separate them, while under ordinary conditions the invisible roughness caused by slight oxidation, abrasion, etc., is sufficient to increase the quantity of air adsorbed to the extent that adhesion is prevented. Fine powders have a tendency to lump together or ball up, which is lacking in coarser powders. This is due to adsorption; and in the case of

(*Concluded on page 552*)

The Ripening of Viscose

Its Industrial Control

What Is Viscose?—The Reaction That Takes Place—Mechanism of Reaction—Difference Between the Different Phases—Explanation of the Phenomenon According to Leuchs—Making the Tests—Conclusions to Be Drawn—Practical Method—Explanation of the Difference—Effect of Other Factors—Practical Test of Method—Comparative Results

By J. FRERE

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Translated by Ismar Ginsberg, B.Sc., Chem. Eng.

THE manufacture of artificial silk from viscose comprises the coagulation of the latter by means of saline or acid solutions or combinations of acid and saline solutions. The coagulation cannot be carried out with any degree of effectiveness when the solutions of viscose have been freshly prepared, but only after they have remained for a certain length of time in a state of rest, that is, after they have undergone a ripening process. The ease with which artificial silk can be manufactured, the mechanical strength of the viscose silk, and in general its common properties are dependent in a large degree upon the condition of the viscose.

What Is Viscose

Viscose is a more or less concentrated aqueous solution of the double xanthogenate of cellulose and sodium, which is called, for short, cellulose xanthogenate. The constitution of cellulose has not yet been exactly defined, but from that ease with which it forms viscose, it may be deduced that it possesses the general hydroxylic properties usually ascribed to the alcohols. For example, ethyl alcohol in the presence of alkaline solutions combines with carbon disulphide to yield sodium ethyl xanthogenate.

In the same manner, when cellulose is treated with concentrated alkaline solutions and carbon disulphide, it gives the double xanthogenate of sodium and cellulose. In both cases it is the formation of the sodium alcoholate that plays an important role in the process.

The Reactions That Take Place

In the case of alcohol, the following equation expresses the reaction that ensues:

$$C_2H_5ONa + CS_2 = CS\begin{matrix}/OC_2H_5\\ \backslash SNa\end{matrix}$$

In the case of cellulose, whose sodium alcoholate bears the name, alkali cellulose, the equation of reaction is as follows:

$$C_6H_9O_4ONa + CS_2 = CS\begin{matrix}/O(C_6H_9O_4)\\ \backslash SNa\end{matrix}$$

A second hydroxyl group of the cellulose then forms another compound with the alkali in excess, so that the group ONa remains in the formula.

Consequently there is formed the compound which has the following formula:

$$CS\begin{matrix}/O.C_6H_8.ONa\\ \backslash SNa\end{matrix}$$

which can also be written as—

$$C_6H_8O_3\begin{matrix}/ONa\\ \backslash OCS.SNa\end{matrix}$$

The sodium ethyl xanthogenate and the sodium cellulose xanthogenate, however, differ in the fact that in their aqueous solutions the first is stable while the second is unstable, decomposing spontaneously on storage. The latter passes progressively through a series of conditions in which the solubility gradually diminishes, ending in complete coagulation.

Mechanism of Reaction

The mechanism of these transformations is a matter of vital importance to the viscose industry, and so it has not been satisfactorily explained. The conclusion is generally reached that the molecule of cellulose xanthogenate undergoes what might be called a gradual polymerization.

The investigations which have been carried out on this matter both by Cross and Bevan, and by Ost, Westoff and Gessner, lead to the conclusion that the first stage of the transformation of the complex xanthongenate consists in the formation of the polymer:

$$\left(C_6H_8O_3\begin{matrix}\backslash OCS.SNa\\ /ONa\end{matrix}\right)_n.$$

This polymer undergoes hydrolysis in two ways. On the one hand there is separated the group ONa, and on the other the group OCS.SNa, with the result that carbonates and thiocarbonates, etc., are obtained. The separation of the group OCS.SNa brings about the condensation of the xanthogenate molecules.

After a period of two days has elapsed the solution contains the xanthogenate:

$$(C_{12}H_{18}O_8.ONa.OCSSNa)n/2$$

The coefficient n/2 is introduced in order to show the relation between this formula and the one preceding, two complex molecules of the first resulting in the formation of the second. Then there is formed the complex:

$$(C_{18}H_{28}O_{13}.ONa.OCSSNa)n/3$$

After a period of five days has elapsed, just before the coagulation of the solution, the xanthogenate possesses the following formula:

$$(C_{20}H_{38}O_{18}.ONa.OCSSNa)n/4$$

Difference Between the Different Phases

The distinction between these different phases consists in the fact that the cellulose xanthogenate, whose constitution is represented by the formula C_6, is not precipitated by saline solutions, nor by dilute organic acid. On the other hand, that derived from the formula C_{12} is precipitated by dilute acetic acid and dissolves in water while that represented by the formula C_{24} is precipitated and is insoluble in water, but is soluble in alkalies.

According to Cross and Bevan there is existent an entire series of xanthogenates leading from a primary form of the compound to the final stage which is cellulose hydrate. The synthesis of xanthogenate requires, in accordance with these writers, agreement with the formula: $C_6H_{10}O_5.2NaOH:CS_2$, which corresponds to the ratio 100:40:40.

When such viscose is precipitated by alcohol or by a salt solution a xanthogenate is obtained whose composition corresponds to the proportion 100:20—20. When it is dissolved and reprecipitated, a product poorer in alkali is obtained and so on, until the end of the transformations is reached.

Explanation of the Phenomenon According to Leuchs

A recent investigation made by Leuchs gives a different explanation to this phenomenon of the ripening of viscose silk. The decomposition of viscose by acids gives rise to the deposition of sulphur and to the evolution of sulphureted hydrogen gas and of carbon disulphide. The sulphur and the sulphureted hydrogen come from the reaction that takes place between the original carbon disulphide and the excess of caustic soda on alkali cellulose. On the other hand the carbon disulphide is formed by the decomposition of cellulose xanthogenate. If the theory of Cross and Bevan is correct viscose during the course of its maturing, when it is treated with acids, should evolve increasing quantities of sulphureted hydrogen and decreasing quantities of carbon disulphide. The relationship between the carbon disulphide and the cellulose should be an indication of the progress of the reaction to which the viscose silk is being subjected.

Making the Tests

In making these tests the hydrogen sulphide evolved is absorbed in pumice stone which has been impregnated with copper sulphate and the carbon disulphide is absorbed by means of activated charcoal, the product first made by the Bayer Company. Leuchs, in making these tests, took the necessary precautions to avoid inaccuracy due to the moisture in the air, by placing tubes filled with calcium chloride at both ends of the absorption apparatus.

The solution of viscose is placed in a flask and decomposed with sulphuric acid, added drop by drop. Then a current of air is gently aspirated through the apparatus, while the liquid in it is heated almost to the boiling point. The free gases are entrained with the air current and pass with it into the absorbing tubes.

The following results were obtained from these experiments:

Days of Ripening	CS_2 to $C_6H_{10}O_5$
Second day	1 to 1.92
Third day	1 to 2.02
Fourth day	1 to 2.13
Fifth day	1 to 1.96
Sixth day	1 to 2.01

Conclusions to Be Drawn

The foregoing figures indicate that the ratio between carbon disulphide and cellulose remained practically constant. Due to this Leuchs derived the conclusion that the ripening of viscose silk is not a pure chemical phenomenon but possesses chemico-colloidal character.

This result is contrary to all that have been found by earlier investigators. It possesses an important bearing on the practical manufacture of viscose silk in that it apparently disqualifies certain methods which have been employed for the determination of the ripening of viscose silk. Among these the determination of the quantity of alkali that is chemically combined is the oldest.

Practical Method

This method depends on the fact that weak acids, such as acetic acid, in coagulating viscose, do not decompose it and do not attack the alkali that is combined with it. Accordingly the viscose is precipitated by a measured excess of acetic acid, the material is

filtered and washed by means of a solution of sodium chloride. It is then a simple matter to determine the excess acetic acid in the filtrate, and the free alkali can be calculated from the difference between the acetic acid found and that which had been added in the first place. A second similar experiment is then made, in which sulphuric acid is employed. This acid totally destroys the viscose, and from this the total quantity of alkali present can be established. The difference between the two amounts of alkali found gives the proportion that is combined and from this figure there may be calculated the ratio of cellulose to alkali.

A study of the ripening of viscose silk by the determination of the alkali combined with it shows a continuous change. A constant quantity of viscose, namely 2.5 grams, was taken as a sample, and the following amounts of alkali were found under different conditions:

	Milligrams of Alkali
1. Fresh viscose before ripening.....	17.68
2. Fresh viscose before ripening.....	13.92
3. Viscose slightly ripened.....	10.96
4. Viscose slightly ripened.....	9.76
5. Viscose slightly ripened.....	7.80
6. Viscose somewhat more ripened....	6.69
7. Viscose ripened	6.20
8. Ripe viscose	5.90
9. Very ripe viscose.....	5.00
10. Very ripe viscose.....	3.60
11. Coagulated viscose	0.08

In the table given above the results are obtained from experiments carried out by Hottenroth and those in the first table were obtained by Leuchs. There is an essential difference between the two.

Explanation of the Difference

The former investigator considers his method to be very accurate and of great value in commercial practice. In searching for other methods just as simple, an attempt was made to apply the colloidal chemical properties of viscose, as the various degrees of ripeness of the silk are distinguished from each other by the varying coagulating action of acids and salts. The differences are likewise gradual.

When the speed of coagulation is measured, it is possible to judge the degree of ripeness of a given grade of viscose. The more ripe the viscose, the more rapidly it is coagulated. This property can be expressed in numerical terms by determining the amount of the coagulating agent required to give instantaneous coagulation. However, the faculty of coagulating possessed by the viscose silk also depends on the concentration of the viscose. Hence, in order to obtain comparable figures, it is essential to work under given conditions of concentration.

Effect of Other Factors

There are a number of other factors which play certin roles in this process. For example, the choice of the coagulating agent is important. Hottenroth used a 5 per cent solution of acetic acid, and found that the amount required for coagulation differed if the viscose was diluted with water or contained varying amounts of sodium hydroxide. However, as the alkalinity of commercial grades of viscose does not vary considerably, it becomes desirable to use a coagulating agent not quite so sensitive as acetic acid. Accordingly, a solution of ammonium chloride was chosen as being most desirable from all standpoints.

Thus, 20 grams of viscose silk are dissolved in 30 cubic centimeters of water and 5 cubic centimeters of a normal solution of sodium hydroxide. In making the experiment two samples of the identical viscose were used, and it was found that in the first case there were required 13.5 cubic centimeters of the ammonium chloride solution and in the second case 13.7 cubic centimeters, the difference being of no consequence.

Practical Test of Method

This method was studied in a practical manner and a series of determinations on industrial viscose solutions in varying stages of ripeness were carried out with it. The viscose was prepared by treating 30 kilograms of cellulose with 128 kilograms of the caustic liquor, thus forming 158 kilograms of alkali cellulose. After standing for a period of 24 hours at a temperature of 25 degrees Cent., carbon disulphide was permitted to act on the mass. For each batch of 340 kilograms of alkalicellulose there were employed 70 kilograms of carbon disulphide. The mass was finally diluted with water or a solution of sodium hydroxide in order to obtain a final product which contained from 6 to 6.5 per cent of cellulose and from 8 to 8.5 per cent of alkali.

In order to determine the degree of ripeness, 20-gram samples were taken during 11 consecutive hours. These samples were diluted with 30 cubic centimeters of water each time the test was made and then the solution was titrated with a 10 per cent solution of ammonium chloride. In each case the amount required for coagulation was noted.

Comparative Results

The results obtained when working with a 5 per cent solution of acetic acid and a similarly concentrated solution of ammonium chloride are given below in tabulated form. It is necessary in order to obtain results that can be equitably compared with one another to work at a stated temperature, as the variation in the temperature has a very decided influence on the process. Coagulation of the viscose solution is accelerated by heat, and retarded by cold. Hence, it is very essential that this condition be carefully controlled.

The results given below are interesting, particularly because of the regularity of change in amounts of the reagents required to effect the coagulation of the viscose silk solutions.

	Acetic Acid	Ammonium Chloride
1. Viscose slightly ripened....	26.5	13.1
2. Viscose slightly ripened....	24.2	12.5
3. Viscose further ripened....	22.8	11.2
4. Viscose further ripened....	19.5	10.1
5. Viscose further ripened....	18.2	9.6*
6. Viscose further ripened....	14.0	8.2
7. Ripe viscose	11.5	7.8
8. Ripe viscose	10.7	6.7
9. Very ripe viscose.....	8.5	5.2
10. Very ripe viscose.....	6.5	4.7
11. Very ripe viscose.....	6.1	3.8
12. Coagulated	...	...

*Optimum.

It was found that a consumption of 9.6 cubic centimeters of an ammonium chloride solution corresponds to a ripeness which is most favorable for the manufacture of silk. It is stated that the author preferred to use a viscose of this type in making artificial silk. The method which has just been described is used to a considerable degree in practical work.

Prescott & Co., of Montreal, have been appointed by the Societe Anonyme des Matieres Colorantes as sole agents for the sale of the French company's aniline dyes and intermediates in Canada. The notice from the Societe Anonyme des Matieres Colorantes says in part:

"We have arranged for this new organization in perfect agreement with Messrs. F. E. Cornell & Co., Montreal, with whom we have been connected many years and who cannot now, on account of the extension of their trade in other lines, devote their time to the sale of our products.

"We seize this opportunity to testify to Messrs. F. E. Cornell & Co. our gratitude for the devotion they have always shown on behalf of our company."

What Do We Know About Sizing Paper With Rosin?

(Conclusion)

Effect of Beating—Kind and Amount of Filler—Nature of Water Supply—Lime Salts in the Fiber—Adding Size to the Beater—Time of Adding Size—Proportions of Size and Alum—Nature of Alum—Alum Substitutes—Operations on the Paper Machine—Thickness of Sheet—Drying Operations—Calendering

By E. SUTERMEISTER

IT is usually thought that fibers which have been subjected to considerable beating are more easily sized than the same fibers in the unbeaten state. This opinion is probably the outgrowth of general manufacturing experience rather than of any carefully conducted series of tests. While such experience is apt to lead to the right conclusion in a general way, yet it does not often explain the reasons for the observed results. In the present instance it is a fairly safe guess that no one knows whether the sizing of all fibers is equally affected by beating or, if not, which are the most influenced. Nor is it probably known whether the effect of beating is progressive or whether the effect is produced during the first part of the beating and to a much less extent during the further treatment. There is a little evidence that this latter statement is true, but it is by no means proven. Neither is there any positive evidence as to whether cutting or brushing the stock affects its sizing more.

Kind and Amount of Filler

The kind of filler has a very important bearing on the sizing results obtained. Under normal conditions good sizing results when clay, barium sulphate, asbestine, calcium sulphate or talc is used, but it has proved impossible to rosin-size papers containing calcium or barium carbonates or magnesia. This is probably due to the alkalinity of the last three materials, though it has not been proved that unusual capillary power or some other factor may not have a considerable influence. With clay it has been shown that the finer the particles the more seriously is the sizing affected; a clay of which 42 per cent stayed in suspension over two hours permitted sizing to an ink flotation test of 170 seconds, while the same amount of clay, 86 per cent of which remained suspended for two hours, reduced the time of penetration of ink to forty-six seconds.

It is a well-known fact that clays vary considerably in their physical properties, of which fineness is one, and it is equally well known that many of the fillers contain varying amounts of impurities, among which

is calcium carbonate. It takes comparatively little of the latter to injure the sizing to a very appreciable extent, which is probably the reason that the producers of a certain kind of filler, which normally contained a small amount of carbonate, formerly recommended boiling it with a small quantity of sulphuric acid before adding it to the beater. Here are two causes of variation in sizing which it is practically impossible to control under actual operating conditions in a mill, and no one can tell just how serious they are or when they are going to take effect. In addition to those there is a third cause of considerable importance in some plants, and that is the use of waste coated papers which may or may not contain calcium carbonate or satin white, both of which are harmful to sizing.

Besides variations in the chemical composition of the fillers or in the impurities which they contain, they are not always retained to the same degree nor can they be used to the same extent in all grades of paper. There is probably little chance of arousing contradiction by stating that the more filler in the paper the quicker the ink will penetrate or the poorer will be the sizing. In two recent tests the following results were obtained:

TIME FOR INK TO PENETRATE

Ash in Paper	Test 1 (seconds)	Test 2 (seconds)
0.5 per cent.....	638	....
1.0 "	..	4,450
2.0 "	430	....
6.0 "	204	2,830
10.0 "	96	1,810
14.0 "	20	1,130
18.0 "	..	775
22.0 "	..	575
28.0 "	..	440

Since the grade of paper determines, to a certain extent, the amount of filler used, variations caused by such changes may be anticipated, but any changes which cause greater or less retention than normal cannot be foreseen in every case and are therefore likely to cause unexpected changes in sizing.

Nature of Water Supply

It is generally conceded that the nature of the water used in paper making has a large influence on sizing results, and the notion is equally general that hard water is injurious. Undoubtedly some hard waters prevent or make difficult proper rosin sizing, but a water may be hard from the presence of calcium chloride or sulphate without being in any way injurious. If, for any reason, the carbonate or hydroxide of calcium is contained in the water the sizing will suffer in proportion to the amount present. The obvious remedy is to neutralize the alkalinity before the size is added, and for this purpose sulphuric acid has been found better than alum. Of course, care must be used not to add an excess of acid, for then it would be merely the exchange of one trouble for another. Schacht recommends the boiling of a small amount of easily saponifiable oil, such as train oil, with the rosin and soda, claiming that such a size dissolves more easily than ordinary size and gives better results.

So much for the mill using a water supply which, while hard, is of practically uniform composition. On the other hand, how about the mill using surface water from a stream contaminated with the waste waters from a number of other industries? Under such conditions variable amounts of impurities will be present at different times, and not only will the amounts vary but the character of the contamination may fluctuate violently. Even where surface water from a farming country is available, variations are likely to occur due to storms and seasonal conditions. Changes such as these cannot be foretold, and they are doubtless the cause of innumerable variations in sizing which are either attributed to other causes or put down among the unexplained happenings of paper making.

Lime Salts in the Fiber

The influence of calcium salts has been mentioned in connection with the water supply and the fillers used. Another cause of such material is the incomplete washing of the bleached fiber, which would then necessarily contain more or less calcium chloride. This is very frequently said to be injurious to sizing, because it causes the precipitation of the rosin, probably in the form of calcium resinate, before the alum is added. This view is held by Schwalbe, Tucker, De Cew and others, but is contradicted by experiments in which very thoroughly washed fiber was furnished with and without the addition of calcium chloride and fully as good sizing was obtained in the former case. This is a rather fortunate state of affairs, for it is difficult to wash fiber entirely free of chlorides and probably all commercial bleached fiber contains enough calcium chloride to be troublesome if it actually injured the sizing. It is possible that the alum sets up secondary reactions which cause the decomposition of the calcium resinate and the formation of aluminum resinate or other compounds possessing sizing properties.

Adding Size to Beater

The old method of adding size to the beater was to measure out so many dippers or pails of the thick size, containing 40 to 50 per cent dry matter, and dump this directly into the stock in front of the beater roll. This worked fairly well while it was customary to use size which was neutral or low in free rosin, but when the free rosin rose much above 25 per cent, trouble was likely to be encountered from the separation of rosin in particles large enough to cause

spots in the finished paper. This difficulty was overcome by the use of some form of emulsifier which enabled dilute solutions to be obtained in which the free rosin was so finely divided that it would not settle out.

In using such emulsions it has been claimed that the concentration has a large influence on the results obtained and that in general it is best to employ dilutions of not over 2 to 3 per cent; one authority even claims that a 1 per cent strength should not be exceeded. There seems to be no question that size is dissociated strongly when diluted with water, and it is possible that in some cases this may have a bearing on the sizing obtained. There is almost no available data relating to this phase of sizing, and what few tests the writer has made were so contradictory that no conclusions could be drawn. Even if it could be demonstrated that a 1 per cent emulsion gave better results than higher concentrations, it is doubtful if it would lead to any beneficial results; for the volume necessary, at least for hard sized papers, would be too great to add to the beater.

Time of Adding Size

There seems to be no fixed rule for adding the size and alum; some mills add one first and some the other; and, of course, each claims to be using the most efficient method. Perhaps each is right, for it is quite possible that conditions in different plants might vary to such an extent that the most effective order of addition should be reversed. The writer's experience has been that the size should be added first and that the alum should be added only a short time before dumping the beater. The diversity of opinion on any sizing subject is well illustrated by the replies to a certain query in which one said add the rosin first, then the alum, and finally the filler; another recommended adding the filler first and the size and alum only just before dumping; while a third said the alum should be added early and before the size. All these opinions were in regard to exactly the same problem.

Proportions of Size and Alum

The ratio of size to the rest of the stock furnished depends on the character of the paper being made, and it may be anywhere from nothing up to 6 per cent. While the amount necessary is influenced by local conditions, such as hard water, degree of beating, amount of filler, etc., nothing would be gained by discussing such problems here. One point that might be brought out, however, is that with papers containing considerable clay nothing is to be gained by increasing the rosin added beyond a certain point, which probably depends on the nature of the furnish.

When it comes to the question of the ratio of alum to rosin an interesting field for speculation is opened up, and much will be found in the literature relating to the various basic aluminum sulphates and resinates which may be formed when different proportions are used. As most of these results are based on the interaction of size and alum without the presence of fiber, they may or may not have some bearing on the actual sizing problem.

Neugebauer claims that 100 grams of rosin in the form of neutral size require 33 grams of hydrated aluminum sulphate for precipitation. With a size containing 31 per cent free rosin it has been found that 100 grams can be completely precipitated with 20.1 grams of aluminum sulphate containing 17 per cent of Al_2O_3. This does not mean that satisfactory sizing will result if these proportions are adhered to, for it has been found from practical experience that far more than this minimum quantity is necessary to give good sizing. Bray states that in the presence of cellulose about two-thirds more alum is necessary to precipitate the rosin than when the cellulose is absent. This may account for part of the difference between the amount of alum necessary to precipitate the rosin and that required for satisfactory sizing, but it certainly does not account for it all, for it has been demonstrated experimentally that alum to the extent of one to three times the weight of rosin used is required to develop full sizing. Smaller amounts of rosin require the greater proportional excess of alum; and as the rosin is increased the excess of alum may be diminished, but under no known conditions may it be reduced to the theoretical amount to precipitate the rosin.

It is evident that little is known as to the reasons why such an excess is necessary nor why the required excess varies so greatly with the amount of rosin used.

Nature of Alum

It is generally claimed that a slightly basic alum is best for sizing, though it is not entirely clear whether the basic portion is at all active as a sizing agent. So far as the writer is aware, there has been no authoritative work done to settle this point, and the claim seems to be based on personal opinions and theories.

The amount of iron which is permissible in the alum is another point on which there is little unity of opinion. There are general standards for the alum for different grades of paper, but it is suspected that they were established by rule of thumb rather than from a knowledge of the actual effect of the iron on the sizing or the paper itself. Until recently it has rather been assumed that ferrous iron would be fully oxidized in passing over the driers and that it was therefore as bad as ferric iron. It now appears that in the ferric state it is taken up by the paper to a much greater extent than when in the ferrous condition. The actual effect on both forms on the sizing still needs a considerable amount of investigation.

Alum Substitutes

Numerous attempts have been made to find a satisfactory substitute for alum, and among the materials

proposed are sulphuric acid, sodium acid sulphate, magnesium sulphate, zinc sulphate and carbon dioxide. Schwalbe finds that rosin precipitated by sulphuric acid does not give permanent sizing, while Remington states that it has little sizing power. Pauli proved that magnesium sulphate was unsatisfactory alone, and that when it was used in mixture with alum the sizing obtained was due to the alum only. Experiments by the writer showed that the precipitate caused by zinc sulphate had no sizing power. While every possible effort has been made to employ these substitutes successfully, the results up to the present have not been satisfactory and alum is still universally employed.

This phase of the sizing game seems to be one of the very few on which there is practical agreement of opinion.

Operation on the Paper Machine

It seems entirely reasonable that the intensity of the suction, the pressure applied to the presses, and the speed of the machine should have some influence on the sizing obtained, but there is apparently no published information showing the specific effects of any one of these factors. The changes which could be made in any one of these to accommodate the sizing would be very slight, because they must necessarily fulfill their primary purposes; but it is possible that a knowledge of how they affect sizing might allow some slight adjustments to be made.

Thickness of Sheet

It is, of course, obvious that the thicker the sheet the longer it will take for ink to strike through; but is the thick sheet therefore really harder sized? If it is considered harder sized, is the increase in direct proportion to the thickness? Is it possible, with a given grade of stock, to predict from the results on a light sheet what the sizing of a heavy sheet would be? Who knows the answers to these questions?

Drying Operations

Of all the operations carried out on the paper machine the drying of the sheet probably has by far the most effect on the sizing. Klemm is of the opinion that the first driers should be only moderately hot; that the heat should be gradually raised to 80 deg. Cent. (176 deg. Fahr.) and then gradually lowered to the end of the bank of driers. He states that the temperature of 80 deg. Cent. must be reached while the sheet is still wet, as dry rosin does not melt at as low a temperature as when moist. Arledter seems to share Klemm's opinion as to the gradations of drier temperatures. Turner finds that above a certain percentage of rosin the effect of heat in the driers is beneficial, but below this percentage it seems to make little difference whether the paper is dried on the driers or in the air at lower temperatures. With very small amounts of rosin slow drying at low temperatures gives the best results.

It has been found that if the wet web of paper is taken from the press and air-dried it is only slightly sized, but if the same web is dried on a steam-heated cylinder very good sizing results at any temperature between 100 and 150 deg. Cent. Better results are obtained it the web is held on the drier continuously than if it is alternately removed and replaced, as it would be in going over a bank of driers. Also, the texture of the felt was found to have an influence, a wool felt giving higher sizing than a cotton canvas. Doubtless the tightness with which the sheet is held onto the hot surface also has an influence.

Granting that these factors are of vital importance, how are tney going to be measured and standardized? We have as yet no satisfactory means of measuring the temperature of the surface of the driers, much less that of the web of paper itself, so how can we be sure that the relative temperatures of the series of driers are correct? How can we be sure that in any given drier the temperature is uniform across its face? How can we be assured that presses, press felts and drier felts are doing their work uniformly across the web? These are just a few of the things that need to be investigated, and when the work is completed perhaps it will be known why variations of 100 per cent or more within 10 inches of each other are not uncommon in a series of tests across the width of the machine.

Calendering

It might be supposed that calendering would injure the sizing because of the physical change caused in a material which has been permitted to set from a more or less plastic condition. This is apparently the case, for out of sixteen samples tested fifteen were found to be more easily penetrated by writing ink after calendering. The decrease in sizing varied from 6 per cent to 43 per cent of that of the uncalendered sheets. In only one case was the sizing better after calendering, and in this case the paper was so slack sized that the results are probably without significance, for the ink penetration time before calendering was only 1.5 seconds and 2 seconds afterward.

So far as known there has been no attempt to develop the relation of loss of ink-resisting power due to calendering, to any of the factors which might influence it, as thickness of sheet, pressure on calenders, degree of sizing before calendering, moisture in paper when calendered, etc.

To anyone who has had the courage and persistence to read thus far, it seems as though it must have been proved that we know very little about sizing and that the field for investigation is very broad but extremely difficult and complicated. Without disparaging in the least the efforts of individual experimenters, it must be evident that their results will be contradictory until

the influence of each factor is so thoroughly elucidated that its effect on their experiments may be understood and corrected for. This is a state of affairs which will not materialize until a very carefully planned attack is carried out under such conditions that there can be absolutely no doubt of the accuracy or completeness of the results. The enormous amount of work necessary to bring this to a satisfactory conclusion almost absolutely precludes handling it in any manufacturing or commercial laboratory, and indicates a Government or university laboratory as the proper place to carry it out. It is very doubtful if any satisfactory arrangement can be made at present to carry out any such extended investigation, and for a long time to come we shall probably have to muddle along with the misinformation which we already possess and what little we can add to it.

APPLICATION OF COLLOIDAL CHEMISTRY TO TEXTILE PROBLEMS

(*Concluded from page 544*)

heterogeneous powders it is noted that the coarser particles adsorb the finer. Thus, in making baking powders it was discovered empirically before it was explain scientifically that the acid element should be relatively coarsely ground, while the starch, which acts as a protective coating, should be very fine. This fact is also taken advantage of in the production of pigments; here the pigment which is desired to predominate in tone should be the finer, the invisible one the coarser.

Coarse Salt for Standardizing Dyestuffs

In standardizing dyestuffs it has been the custom to use very finely ground salt; this shows an ignorance of physical laws. The salt in a dyestuff is much less conspicuous if the dyestuff is much more finely ground than the salt, and then the two should be stirred together, not ground together. Soiled fabrics may represent adsorption of solids by solids, but more frequently there is adsorption of liquids by the fiber surface, usually of greasy nature, which displaces the adsorbed air on the surface, and then on the greasy surface the dirt particles are adsorbed. The action of soap as a detergent is to emulsify the grease, and the interfacial surfaces surrounding the globules of grease prevent readhesion to the fiber. Particles of dirt may be found in the interfacial surfaces and promote the emulsification.

Indeed, so familiar are the examples of applied colloid chemistry that there is the danger, already alluded to, of merely saying what is perfectly well known in difficult language: thus, to say, what is perfectly true, that one is going to perform an experiment in colloidal chemistry when he goes to wash his hands or write on the blackboard is affectation, yet consideration of these everyday occurrences in the light of the new knowledge of colloid chemistry may give light on other problems whose solutions are now remote.

Colloid chemistry is thus the study of how the reactions of chemistry are modified by the size of the reacting substances. As these diminish, the effect of the molecular forces is more pronounced; as the aggregate increases, the effect is less pronounced. With molecules, reactions are quantitative, because the electric molecules are unit charges or simple multiples thereof; but as the molecules are agglomerated a greater or less proportion of the charges is neutralized in intra-aggregate relations, and phenomena like those of adsorption take place which are modified by external molecular conditions, but at the same time are not quantitative because of physical conditions.

THREE NEW INSERTS FOR NEWPORT BINDER

Three new technical bulletins have been issued by the Newport Chemical Works as supplementary inserts for the binder they recently distributed. The complete set of inserts for this binder now numbers seven.

Two of the new bulletins treat of a product known as Hydraphthal. The first gives a brief survey of the properties and uses of the product, which is used in scouring and degreasing operations. The second bulletin on Hydraphthal gives more complete information and tells of its use in the wool and worsted industries. The bulletin describes the use of the product in wet finishing woolens, comparing its use with that of soaps and alkalies. One section gives general instructions for the use of Hydraphthal and takes up in turn its use for primary washing, milling and scouring of dress goods, pure worsted goods, piece dyed worsteds, ladies' high-grade cloth and woolen and half woolen blankets.

The third bulletin describes the properties of two new products known as Neomerpin and Neomerpin-N, the use of which permits easier manipulation in the application of vat colors and other dyestuffs on textiles.

The Taylor Instrument Companies are mailing to their customers a folder describing a new instrument they have recently placed on the market, called "The Stormaguide, a weather counsellor for golfers and all outdoors' people." The folder, which is handsomely printed, with a steel-engraved cover design, contains a photograph of the instrument, which has a five-inch silver metal dial set in a polished mahogany stand 14½ inches wide at the base.

Dr. W. W. Sands, city clerk of Kingston, One., announces that the directors of the Canada Dye & Chemical Company have taken over the agreement between the City of Kingston and Dr. Atack, chairman of the directors of the company, and that the work of erecting the plant is to be commenced in September.

Proceedings of the American Association of Textile Chemists and Colorists

The American Association of Textile Chemists and Colorists

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OUTING OF THE NORTHERN NEW ENGLAND SECTION

About one hundred members and guests of the Northern New England Section of the American Association of Textile Chemists and Colorists gathered at the Merrimac Valley Country Club near the town of Methuen, Massachusetts, on July 10, to participate in the annual outing of the Section. The entertainment committee is to be congratulated upon the successful manner in which it carried through all of the plans for the day. The events of the afternoon and evening had been so carefully arranged that when the day was over and the guests were leaving, everyone heartily agreed that the outing had proved far more enjoyable than even the most optimistic had been led to expect.

Games of golf, tennis, baseball and quoits filled out the program for the afternoon, and with this diversity of amusements each had his opportunity to indulge in his favorite sport. Everybody visited and chatted with everybody else and did his best to spread the general sociability and the feeling of good fellowship which pervaded the various features of the day.

William R. Moorhouse, acting as "sheriff" and S. R. David as umpire contributed much to the enjoyment of the lively baseball games in their sincere endeavors to guide the capricious whims of the spectators and players. These two energetic officials afterward consumed a goodly portion of their dinner, greatly to the surprise of the others who supposed that they would be unable to return to normal for some time.

In the baseball games the Dye Salters, ably captained by Frank McCool, emerged champions of the day after defeating the Dyer Dams in the preliminaries and the heretofore victorious Scofflaws in the finals. The Scofflaws, elated by their victory over the Mill Chems, fought hard for the trophy, but, although their score mounted steadily, they failed to total a winning figure.

At seven o'clock the rumor that dinner was waiting caused a sudden "grand obstacle chase" to the dining room at the clubhouse. Chaos was reduced to order under the bracing inspiration of music. Albert Sampson, ably accompanied at the piano by John Dalton, was highly successful in persuading the expectant diners to join in the singing. The resultant music added a pleasant flavor to the good things that followed.

After the dinner Professor Louis A. Olney introduced Colonel H. A. Metz of H. A. Metz & Co. The members and guests felt exceedingly honored by the presence of Colonel Metz and sincerely appreciated his brief talk on co-operation within the dye industry.

Colonel Metz emphasized his hearty praise and approval of the Association, characterizing it as a laudable move toward the ideal of the industry: co-operation and mutual understanding. "We are all gentlemen," he said, "and should meet like gentlemen and act like gentlemen, and refrain from the undue criticism and censure that makes for ill feeling and dissension." He denounced as "rot" some of the propaganda, circulated during the war, insinuating dishonesty and corruption among the factions in the American dye industry. He declared that the few in every industry who are guilty of dishonest methods

(*Continued on page 556*)

Above—Group with Professor Louis A. Olney.

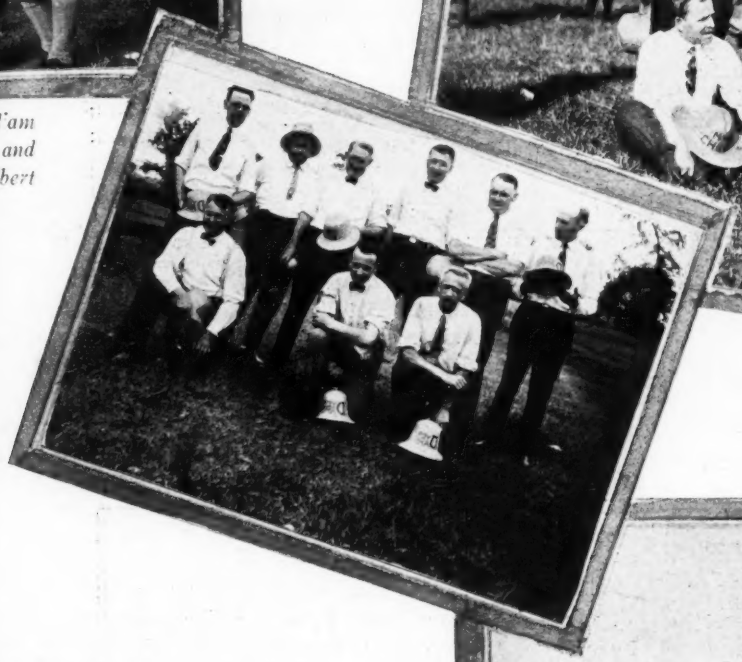
Right. — The Scofflaws, contenders for the title.

Below — The Dye - Salters — Champion Ball Players.

Sheriff R. Moorho Chairman Sampson

The Umpire, S. R.

Sheriff Will'am R. Moorhouse and Chairman Albert Sampson.

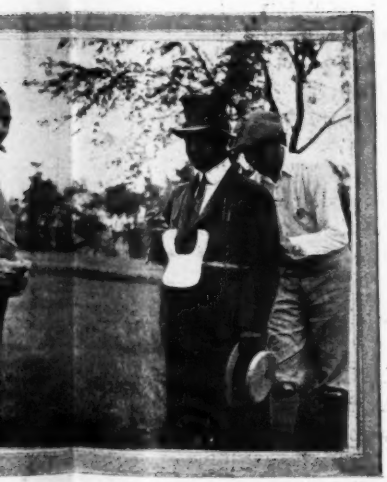


Above. — The Mill-Chems Ball Team.

Left. — The Dyer Dams.

Below—Group with Colonel H. A. Metz.

ire, S. R. David, Rigging Up



(*Continued from page 553*)

should not be regarded nor held up as typical of that industry. He stated that the United States now has a dye industry that it can easily control and foster to an enviable maturity, but that the industry must stand upon a solid bedrock of mutual confidence and friendly agreement among its individual members. He gave it as his opinion that in the past there has been too much criticizing of the other fellow and his methods and not enough of the close co-operation so desired by the majority; but happily, he said, recent activities of dye and chemical associations in the country plainly attest to the growing mutual understanding and confidence within the industry.

William H. Cady was called upon to announce the prize winners of the athletic events and to distribute the valuable prizes. These awards were accepted by the winners with dignified gratitude amid the applause.

During the brief but interesting business session held to announce the results of the balloting for the officers of the Section Hugh Christison presided. The results of the election gave as officers for the following year: Chairman, John Bannan; treasurer, Miles R. Moffatt; members of the executive committee for two years, Hugh Christison and George Stewart; secretary, Arthur K. Johnson.

Before dispersing the Section expressed to the committee its sincere appreciation of the occasion. The outing was in charge of Albert E. Sampson, chairman, Leverett N. Putnam, Frank Johnson, Louis Bume, William H. Cady and Hugh Christison.

Throughout the afternoon photographers, official and otherwise, were much in evidence endeavoring to secure picture records of the occasion. Unfortunately, many cameras were lost in the excitement and several others were forgotten by their owners after the first exposure. However, several films were salvaged and reproductions of these shown herewith will serve to give some idea of the nature of the festivities.

CHANGES OF ADDRESS

Clement, D. Scott, 88 Broad Street, Boston, Mass.
Franke, K. W., 897 Portland Avenue, St. Paul, Minn.
Goldthwait, Charles F., 29 Euclid Avenue, Waterbury, Conn.
Kittridge, Roland F., 7 Spring Street, Willimantic, Conn.
Krebe, Charles G., P. O. Box 142, Franklin, Mass.
Linte, Leonard S., care of Pacific Mills, Wellford, S. C.
Marsden, William, 59 Park Street, North Andover, Mass.
Masson, John G., 45 Trent Street, Woonsocket, R. I.
Taylor, Oscar C., Fourth and Saville Avenues, Eddystone, Pa.
Walsh, George, 454 Park Avenue, Weehawken, N. J.
Worthen, C. T., 46 Jewett Place, Utica, N. Y.
Young, Fred L., care of Grasselli Dyestuff Corporation, 117 Hudson Street, New York.

APPLICANTS FOR MEMBERSHIP

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Alston, John, superintendent, Farwell Bleachery, Lawrence, Mass. Sponsors: G. W. Aspinall and H. D. Grimes.

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Hirsch, L. S., manager, B. P. Ducas Company, Inc., New York City. Sponsors: W. W. Hales and S. Klein.

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Williams, Charles, Overseer of Dyeing, Renfrew Manufacturing Company, Adams, Mass. Sponsors: Alden D. Nute and Ben Verity.

Junior

Palmer, Ray E., chemist, Atlantic Mills, Providence, R. I. Sponsors: R. F. Culver and J. J. Sokolinski.

Schmatzler, Karl H., assistant dyer, National Aniline & Chemical Company, Boston, Mass. Sponsors: H. F. Finlay and A. K. Gyzander.

Sweet, George A., Second, textile apprentice, U. S. Finishing Company, Pawtucket, R. I. Sponsors: N. Barlow and W. Milne.

ASSOCIATION BADGES

Those who attended the Annual Meeting at Providence had an opportunity to examine and purchase the new lapel button badges which were there distributed by the Secretary.

For the benefit of members who were unable to attend the meeting an illustration of the badge is shown herewith.

The three "rings" are enameled in red, yellow and blue, respectively, and the initials and border are brought out in gold. The general effect is exceedingly attractive.

Badges may be secured at $1.50 each by addressing the Secretary.

WALTER E. HADLEY,
5 Mountain Avenue,
Maplewood, N. J.

AMERICAN
DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

LOUIS A. OLNEY
PROFESSOR OF CHEMISTRY AND DYEING, LOWELL TEXTILE SCHOOL
Directing Editor

CLAYTON HOAGLAND
Managing Editor

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THE LABORATORY A PARTNER IN ADVERTISING

THE advertising department of every textile corporation should use its laboratory. With the present-day tendency toward educational advertising, and with the laboratory one of the best sources of educational information in the whole organization, there is no good reason why the laboratory should not be asked to co-operate to a far greater extent than is usual in furnishinging advertising material. We are not thinking of the advertisements in The REPORTER, for they necessarily have a great deal to do with laboratories, and are a case by themselves. We are thinking rather of the textile mills which are bringing their wares to the attention of the general public.

A few national advertisers feature their laboratories or the results of specific experiments. To a certain extent this method of advertising is, perhaps, also an experiment, but there are a few cases where it has been continued over quite a period of time so we can conclude that when properly done it is successful.

We doubt if general remarks to the effect that the wonderful research organization is searching far and wide for new things, will amount to anything. On the other hand, even the commonplace facts in most industries are totally unknown to persons not engaged in them, and when briefly and simply presented they are interesting. The fact that routine tests are made on deliveries of dyestuff to see that quality is maintained, is news to most people and can be made into an interesting bit of evidence that the products on which they are used are necessarily among the best. Nor do we have to limit the data to dyeing, for routine tests are often made on the strength of yarns or their size to insure uniformity and high quality in the final product, all evidence of care on the part of the manufacturer and an assurance to the customer that he is getting what he deserves.

Visitors enjoy going through a plant and usually everything is new to them. A series of short stories planned like an explanation of a visit to the factory can be easily worked up and there is, or should be, no one better qualified to assist in a suitable choice of material and in writing a correct account of what is going on than the laboratory director. Such things will also appeal to people who are already familiar with the mill work, or who may have worked in mills themselves, for we all like to unexpectedly come upon things that we already know. As to the rest, the average person knows little enough about cotton, wool or silk. The simplest kind of information about the sources of fibers and their characteristics, as well as how fibers are made into yarns or how yarns are woven into the wonderful variety of fabric found in the department stores, has already been found in conversation to be interesting to many people, and properly presented would no doubt appeal to a larger audience.

The up-to-the-minute laboratory has a great store of facts about the raw materials and how they compare with other things of similar use. It knows a great deal about the uses of the product and their advantages as compared with other things of similar use. Copy written around any unusual data from the laboratory archives has a special appeal.

Laboratories can assist greatly in preparing educational as well as interesting exhibits of products or materials at different steps in the process, by making comparative tests of strength or fastness, or preparing directions to aid the customer in getting the best possible service from the goods. Suggestions on the methods of cleaning have already become quite common and have no doubt had a good effect in teaching housewives that they cannot wash everything like a pair of overalls. Even simple qualities that the goods should have can be presented in a new light or simple tests that they should meet.

Perhaps these particular things have been done, but they are only mentioned as suggestive of possibilities for direct consumer advertising.

Advertising managers are always looking for striking facts to feature, for large spaces full of generalities are not convincing to the reader and do little more than keep a name before the public. Far be it from our thought to start a campaign to educate the public either by force or by letting it steal gently upon it ere it is aware, but the presentation of a little sound logic based on a simple experiment or of a few plain facts is apparently gaining ground as a means of arousing interest.

Whether it is a passing fad remains to be seen but we believe that so-called educational advertising is on the increase and has come to stay. If it has not yet occurred to the advertising manager to enlist the services of the laboraory staff, not necessarily to write copy, but to supply interesting and accurate information, perhaps it is time for the latter to step forward and see if a little more interest cannot be created.

The suggestion is made because such co-operation has

been tried and found useful. Incidentally it forms one more point of contact between the laboratory and the front office, where there always seems to be an opening for more appreciation. It must not, however, be regarded as just another job, but should be recognized as an opportunity and undertaken with enthusiasm.

FOREIGN DYE FASTNESS MAY NEED TO BE PROVED

FASTNESS of dyes is a subject that will lend itself to discussion as long as dyes are made. We are pleased to note the housewife's opinion that the dyes in present-day goods are better than they were several years ago. It reflects deserved credit on American dye manufacturers.

Our thoughts on this subject, however, were set in motion by a news (?) item which may or may not be more than a bit of superheated atmosphere. It is rumored that the fearsome "I. G." is going into the "gents' furnishings" business and will start a chain of stores, perhaps on the order of the A. & P. or another Piggly Wiggley, but at any rate to prove the superior —or, we should say, the supreme—quality of their famous dyes.

If we have reached a stage where these things must be proved, perhaps that is just cause for further congratulations to our own producers.

There was one little provision to the housewife's remark that is perhaps more than half the story: "—if you are careful in washing them." If we consider almost any important type of fastness the same provision applies; for even though we have fast dyes, commercial shades have to be made of combinations and in such combinations there is very often at least one weak sister. The same is true in any range of colors; some are almost certain to be faster than others. Rather than boast too much about the best, it is wiser to caution the user about undue exposure or too severe washing; for the first step in the struggle for fastness is that reasonable requirements be reasonably well met The dyes of extra fastness will take care of themselves, but if they do not fade consistently with the rest they may do more harm than good.

Goods can be made, and made with American dyes, to stand severe requirements, and the conditions will be met on demand. ("Demand" is defined in economics as desire plus ability to pay.)

Ordinary goods should not have to encounter the severest tests unless designed for the purpose. Some of the draperies and other sun-fast materials made in the United States are eminently satisfactory and actually better than foreign goods. Reports on the good quality of American dyeings are more frequent. If the effort is made to feature fast goods, there is not only extra manufacturing cost but it may entail a large additional advertising expense to get proper recognition. However, the tendency is now in the right direction and the rumored German effort suggests that neither dye nor textile manufacturers are in any danger of going too far.

T. C.'S COLUMN

THE "T. C." A JACK-OF-ALL-TRADES

A TEXTILE chemist should know a lot of things and be ever ready to learn a lot more, especially about mill equipment. The school has not time to teach everything, and there may not always be mechanics, electricians and engineers within easy calling distance. To the would-be textile foreman, dyer or superintendent the necessity for a knowledge of machinery is quite evident, but the laboratory chemist may have a different point of view.

One in the laboratory does not often find it necessary to give thought to such things, for in a large plant there are always men on hand to take care of these details. However, things that are mere details in a big plant assume very great importance in a small one; and some of the best experiences and opportunities leading to positions as plant executive can be found in these smaller places, where it is a case of "do or die." If a hydro-extractor goes out of commission, and it is the only one there is, it may easily mean that production will stop, and if one does not already know what that means he will soon find out.

Any ambitious laboratory man wants a closer connection with the mill, and he cannot get very far without becoming responsible for something out in the plant; whether it is a little responsibility in a big place, or a relatively greater responsibility in a small place, it will probably involve the supervision of machinery, pipe lines, and motors, if not elevators and boiler plants. Unexpected opportunity may put one right up against these engineering problems.

Generalizations are not interesting or convincing, so we will fall back on personal experience and suggest in some detail typical problems of this nature that were encountered in working from the laboratory into the mill in different small plants where the desired kind of expert help was not always available.

Should a textile chemist know anything about boilers? Perhaps not, if all he is called upon to do is to open a steam valve when he wants to use steam. On the other hand, if he is fortunate, or unfortunate, to be superintendent of a small plant the case becomes different. It will usually be found that the firemen one can afford to hire in a small place are in the class of those who could know more about their business. No two of them do things alike, which is evidence enough that they are not all correct, and they are constantly neglecting something here or there, which,

if not positively dangerous, will at least make the mill burn too much coal.

When electric motors run it seems as though, like a brook, they would go on forever; but the bearings wear faster on the lower side where you cannot see them. Some day the motor will begin to scrape, and then watch out for trouble. The danger is that you will have not only a repair bill but possibly a disastrous shutdown. A periodic test with a gauge will tell when the danger point is being approached.

How about the starting box? What is the little contraption on the side? Does any part of it need oil and how often should it be inspected and renewed? An electrical machine is like the human system—little troubles accumulate until all at once something stops. Knowing when to fuss with a motor and when to shut it down is much like knowing when to go to a doctor.

Why need a slip ring motor for certain uses; how should it be taken care of? It is obvious that many details like this are discovered only when something gets out of order.

It is a good thing to get the feel of machinery, to handle the valves, shift the belts, and throw on the juice; but learn to do it without smashing the steam lines with water hammer, throwing off all the belts, or making the motors jump off the base plates. Gently, but firmly, is the rule, unless you know the eccentricities of each particular contrivance.

An ordinary hydro-extractor is about as foolproof as any piece of apparatus, and still about as dangerous. What is the manufacturer's rated speed, and how do you know what it is running at that figure? The little things cause the most trouble, however. The brushes begin to spark and the slip rings get rough. If they are not attended to at once, we have to stop and send the motor out to have them turned down smooth again, resulting in a delay of perhaps several days, and a loss of more than several dollars.

Extractor operating has always seemed dangerous, and I often wonder why the manufacturers do not send out more information about the care, loading and starting of these machines, and wonder, too, that more of them have not caused serious accidents. They are well designed, however, and now, with push-button, two-minute starters, or whatever they are, and with the still more modern "humatic" and automatic controls, they are safer than ever before.

When undertaking the supervision or operation of new machinery it is always well to write to the manufacturer for information. Such inquiries will receive careful attention, for any manufacturer wants his machinery to give the best possible service. By writing, one can easily check up on the proper care; may learn of details, like places to oil, that were never guessed to be there; or obtain good operating suggestions, often the result of others' practical experience.

The simple matter of lubrication is very important. Oiling at the bearings and slopping oil all over the machine should not be countenanced. The oil is needed, with very few exceptions, wherever two pieces of metal rub together. Using just enough in the right places, and seeing that it stays put, are not only essential for saving oil, but to help keep unsightly and troublesome oil stains off the goods.

The proper choice of materials of construction is one of the most important matters in any textile plant where chemicals are used. When everything is all set up, you may not have to worry about that subject for a long time, but if you are helping to design an addition to the plant, questions arise which are often very puzzling. We can but suggest a few possibilities. What kind of pipe should be used to carry bleaching solution from stock to the bleach tubs? If bleach is to be circulated through the goods, what kind of pump and what metal fittings will be best, considering endurance as well as the initial cost of the installation? If it is necessary to circulate sour through the system, will that change the materials? There are similar problems in connection with mercerizing, carbonizing, and all other chemical operations, including the various kinds of dyeing.

There are innumerable other questions of minor importance: Whether minor ground joint or gasket unions should be specified; which kinds of quick-opening valves will give the best service; what temperature controllers are best; how to specify lumber and structural steel; how to tell when gears are so worn as to need replacing; and so on, without number.

Such information cannot all be found in any one place, and a great deal of it cannot be found in print. The only way to acquire it is to see and hear, and ask questions wherever they will not be resented. Next best to knowing is knowing enough to find out.

T. C.

The American Chamber of Commerce in Germany announces the publication of the 1924-1925 edition of the American Buyers' Guide, which comprises more than 2,250 names of German manufacturing, import and export firms, banks, forwarders and agents, alphabetically arranged, showing address, branch of business, and names of American representatives. Articles of merchandise form another alphabetical and classified section with sources indicated. The object of this guide is to give American manufacturers a classified directory of importers and sources of supply, and at the same time complete hand-book information related to buying and selling in Germany.

A recent circular distributed by the Chemical Division of the Department of Commerce contains a list of new pharmaceutical preparations which have been produced in Germany recently. Ninety-six different products are listed. This data was compiled under the supervision of C. C. Concannon, Chief of the Division.

FALL MEETING, AMERICAN CHEMICAL SOCIETY

Scientists of the United States, Canada and Europe will gather at Cornell University, Ithaca, N. Y., September 8 to 13, to discuss at the fall meeting of the American Chemical Society the world's progress in chemistry and allied pursuits. Universities and industrial enterprises in every State will send more than 1,000 delegates.

England, among others, will send Sir Robert Robertson, president of the Faraday Society, and Sir Max Muspratt, one of the leading industrial chemists of Great Britain. A group from the Continent will include Prof. S. P. L. Sorensen, of Copenhagen, a leader of the academic school, and internationally known for his work on the hydrogen-ion, of which he is the father.

Chemistry's growing importance to civilized society will be the underlying theme of the second day of the Ithaca conclave, at which the triumphs in chemistry of many nations will be told. "Chemistry and Civilization" will be the topic of Sir Max Muspratt, vice-president of the Society of Chemical Industry.

Sir Robert Robertson, authority on explosives and long in the service of the British Government, notably at Woolwich Arsenal, will describe the nature and use of T. N. T., his formal topic being "The Chemistry of the Trinitrotoluenes."

The general meeting at which the foreign chemists will speak will be held on Tuesday, September 9th, at 9.30 A. M. in Bailey Hall, Dr. Livingston Farrand, president of Cornell University, presiding. A response to addresses of welcome will be made by Dr. Leo Hendrik Baekeland, of New York, president of the American Chemical Society and professor of chemical engineering in Columbia University. On the afternoon of this day the visiting chemists will inspect the Baker Laboratory, the gift of George F. Baker, of New York.

Discussion of the nation's fuel supply will be one of the biggest features of the meeting, according to Dr. Baekeland's announcement. Secretary Hoover's plans to relieve coal shortage and the report of the Coal Storage Committee of the American Engineering Council, will be dealt with.

The Division of Industrial and Engineering Chemistry will hold a two-day symposium on "Absorption," at which papers involving theory and practice will be presented, according to the chairman, Prof. W. G. Whitman of Massachusetts Institute of Technology.

The chemists will assemble, it is pointed out, with America still holding the leadership in chemical research which she took from Germany during the World War, and with clear evidences of an unprecedented forward movement in the whole field of chemistry, as indicated by the many millions of dollars now being raised by universities for enlarged resources in instruction and inquiry.

U. S. FIRMS ADOPT FAST DYE BRANDS AS TARIFF DROPS

In anticipation of the threatened invasion of American markets by German manufacturers due to set in September 1st, American manufacturers are mobilizing an array of trade-marks, according to a survey made by Munn & Co., patent and trade-mark attorneys, of New York City. This is especially true in all textile lines. Munn & Co. alone in the last week have received more than sixty inquiries for trade-marks which shall express permanent colors. These inquiries come from a score of the biggest firms in the business.

On September 1st, the present import duty of 60 and 7 for German dyes is replaced by the new duty of 45 and 7. An influx of German dyes is considered certain to follow the introduction of the lowered duty.

German dyes heretofore have enjoyed a reputation for being fast colors. American dyes, unfortunately, have had the reputation of being of lower quality and not permanent. Despite the tremendous strides forward made by the dye manufacturers of this country, reaching a point where many persons believe they now equal the German product, there still persists a widespread impression that the best dyes are German dyes.

When the new flood of German dyes reaches this country, beginning with next month, it is expected there will be considerable propaganda favoring the use of fast colors, and that permanency of the dyes in fabrics of all classes will be one of the leading selling arguments advanced. In anticipation of this American firms dealing in knitted goods, silks, carpets, laces, tapestries, woolens, cotton goods, linens and other lines are applying for trade-marks that imply colors that will not run or fade.

Such marks as "Permafast," "Permalawn," "Permacolor," "Fastdye," "Shrunkfast," "Fastones," "Sunfast," "Fadeproof," "Neverfade" and "Mellochrome" are included in the veritable lexicon developing in the offices of patent and trade-mark attorneys. Most of the trade-marks consist of the word "Perma" in association with some other word, like fast, color or tone. They are intended to be applied to fabrics made and dyed in this country, the idea being to convey the impression of permanent color, irrespective of the country of origin of the dyes. In this way the American manufacturers are endeavoring to steal the German thunder before it begins to reverberate.

When the actual importations of dyes begin, a favorite method will be, it is said, to make up the compounds in Germany in a manner sufficiently complete to be exported to this country in bulk. After arrival in this country they will be further perfected into final form and then sold under trade-marks or brands.

This enables the German manufacturers to secure low duties on imports in bulk, and at the same time obtain a high price for the perfected and branded product. Trade-marks already are being taken out in the names of the local agents in this country.

Use of Soda Ash in the Beater Coloring of Sized Papers

Acid Dyes—Soda Ash Treatment with Acid Dyes—Basic Dyes—Comparison of Methods of Dyeing—The Soda Ash Treatment with Basic Dyes—Conclusions

By WALTER C. HOLMES, Ph.D.

IN a recent article by Mann[1] on the coloring of paper the employment of soda ash in the beater is recommended in the dyeing of bleached stock with basic dyes, and of both bleached and unbleached stock in deep shades with acid dyes. The formulae specify the use of from 2 to 3 per cent of soda ash (based upon the amount of stock) with basic dyes, and from 20 to 40 pounds with acid dyes, together with proportional increases in the amount of alum employed. The practice advocated is essentially novel, and it is doubtful if it will find ready acceptance in the trade in view of the prejudice which is prevalent against the use of soda ash in the beater.

It is the purpose of the present paper to summarize various results obtained by the writer in experimental laboratory dyeings[2] which afford evidence of the effectiveness of the use of soda ash in this connection in promoting the retention of acid and basic dyes.

Acid Dyes

Although Huebner[3] has obtained interesting data on the absorption of two acid dyes on various types of paper materials, which demonstrate that moderate amounts of dye may be taken up under conditions which are not fully specified, the degree of direct absorption of acid dyes, in general, in customary beater practice is relatively inconsiderable with unbleached stocks and practically negligible with bleached stocks.

It is only by reason of the fact that acid dyes are precipitated as insoluble salts by alum that their employment is feasible in the beater coloring of sized papers. The degree of precipitation under beater conditions, however, is ordinarily far from complete, as is, also, the degree of retention of the precipitated dye salt by the sheet.

In the following table are recorded percentages of Orange II removed from solution, in one form or another, under a variety of conditions. The conditions of the tests were such as duplicated 12-pound dyeings on 1,000 pounds of stock with 12, 30 and 40 pounds, respectively, of soda ash, size and alum. The residual dye was determined in the filtered solution by means of titration with titanous chloride.

[1] Dyestuffs (1922), **23**, 935.

[2] Carried out at the technical labartory of the Du Pont Company in 1921.

[3] J. Soc. Dyers and Colorists, May, 1922.

It should be noted that the behavior of acid dyes is individual in numerous respects, and that the tabulated values are to be accepted as applying only to Orange II. It will be evident, moreover, that the recorded data do not afford a reliable index of the results obtainable in actual dyeings, since variable proportions of precipitated color might escape retention in the sheet.

TABLE I

Percentage Removal of Orange II from Solution

	In Absence of Stock	With Bleached Sulphite Pulp	With Ground Wood
Dye alone	....	2.7	19.1
Dye + alum	23.1	22.4	65.0
Dye + alum + soda ash	57.7	58.5	55.6
Dye + soda ash + alum	57.0	57.7	57.0
Dye + size + alum	35.7	29.3	72.9
Dye + size + alum + soda ash	58.0	65.5	57.5
Dye + soda ash + size + alum	73.4	77.7	78.4

In order to obtain as reliable evidence of the practical effectiveness of various dyeing provisions as is possible in laboratory practice, further and more comprehensive series of laboratory dyeings were carried out. Particular attention was given to maintaining uniform suction in forming the dyed sheets and all results were confirmed in duplicate dyeings. The relative rating of methods recorded in the following tables was established on the basis of comparison of the tinctorial strength of the dyed sheets. Methods 1 to 6, inclusive, do not provide for the sizing of the paper and are included merely to render the data more complete.

TABLE II

Acid Dyes on Bleached Sulphite Stock

Number and Method	Nigrosine WSB	Scarlet 2RL	Oran. II	Aver. Rank
1. Dye alone	11	10	10	10
2. Dye + size	12	11	12	12
3. Dye + alum	9	9	9	9
4. Dye + soda ash + alum	7	5	3	5
5. Dye + alum + soda ash	4	6	8	6
6. Dye + soda ash	10	12	11	11
7. Dye + size + alum	8	7	7	8
8. Dye + alum + size	6	8	5	7
9. Dye + alum + size + soda ash	1	3	6	4
10. Dye + soda ash + alum + size	5	1	2	2
11. Dye + size + alum + soda ash	3	2	4	3
12. Dye + soda ash + size + alum	2	4	1	1

TABLE III
Acid Dyes on Ground Wood

Number and Method	Nigrosine WSB	Scarlet 2RL	Oran. II	Aver. Rank
1. Dye alone	11	11	11	11
2. Dye + size	12	12	12	12
3. Dye + alum	5	9	5	8
4. Dye + soda ash + alum	9	3	9	9
5. Dye + alum + soda ash	6	2	3	2
6. Dye + soda ash	10	10	10	10
7. Dye + size + alum	7	8	2	6
8. Dye + alum + size	3	7	4	4
9. Dye + alum + size + soda ash	1	6	8	5
10. Dye + soda ash + alum + size	6	4	6	7
11. Dye + size + alum + soda ash	4	1	7	3
12. Dye + soda ash + size + alum	2	5	1	1

The best average results were obtained by the employment of soda ash, size and alum, added after the dye in the order given (Method No. 12), although it is indicated that the order of the addition may be varied with advantage with individual dyes and stocks. This method will be referred to subsequently as the "soda ash treatment." It invariably gave decidedly stronger dyeings than did Method No. 7, which finds extensive application in the trade in dyeing deep shades with acid dyes. The latter method will be referred to as the "usual method," although it will be understood that trade practice varies considerably in different mills.

Soda Ash Treatment with Acid Dyes

It was found advisable to modify the proportion of soda ash in the original formula. Two formulas were adopted on the basis of laboratory tests; the first specifying 8 pounds of soda ash, 30 pounds of size and 40 pounds of alum, and the second, which is adapted to provide a lighter sizing, specifying 15 pounds of soda ash, 20 pounds of size and 50 pounds of alum. The first of these formulae, in particular, was given a very thorough test by comprehensive laboratory dyeings against the usual method.

The effectiveness of the soda ash treatment varied with different paper materials. With bleached soda stock it proved slightly detrimental while the opposed provision of increasing the amount of alum proved slightly but distinctly beneficial. The improvement which it effected in the coloring of ground wood was only moderate. In the dyeing of bleached rag stock, however, as well as that of sulphite pulps, whether bleached or unbleached, it was of very decided benefit.

The improvement in color retention was general for dyes of the acid class and extended even to pigment colors of acid characteristics, such as the Heliopont lake colors. In forty-eight acid dyes investigated no exception was found.

The degree of improvement in dye strength was comparatively moderate in the instance of a few dyes which give the most satisfactory retention in the usual practice but was decided with the great majority of dyes tested. The degree of improvement was also found to be dependent upon the depth of the shades run, being inappreciable in light dyeings but increasing with the amount of dye employed.

The order of improvement effected with numerous dyes may be illustrated by citing the results obtained with Orange II. On bleached and unbleached sulphite stocks the improvement was negligible in 2-pound dyeings and only moderate in 4-pound dyeings, but amounted to about 50 per cent when larger amounts of dye (8 to 16 pounds) were employed. An 8-pound dyeing with the soda ash treatment on sulphite or rag stock proved fully equal to a 12-pound dyeing by the usual method.

In general the alteration in shade, resulting from the use of soda ash, was not considerable. In no instance with the dyes investigated were the modified shades appreciably duller or less attractive than the usual shades. On the other hand, considerable improvement was obtained with Metanil Yellow, Fast Red A and certain other dyes. With the dyes of the eosine group bright yellowish shades were obtained, of which those of Phloxine B and Rose Bengal were decidedly stronger and more attractive than their ordinary shades.

General improvement was observed in respect to two-sided effects.

Basic Dyes

The nature and mechanism of the color retention of basic dyes in the beater is essentially different in the case of bleached and unbleached materials. With unbleached stocks the predominant factor in the coloring is that of lake formation between the dye and acid components present in the stock.[4] The natural affinity of such stocks for basic dyes is so considerable that it may give rise to localized overdyeing (with consequent mottling) in the absence of suitable precautions, and it is only in the dyeing of very deep shades that serious difficulty may be encountered in effecting a satisfactory retention of color.

With bleached stocks the predominant phenomena appear to be those of surface absorption, modified, in the coloring of sized papers, by lake formation with the sizing material. The percentage color retention in unsized dyeings is seldom satisfactory except in very light dyeings, and it is by no means easy to obtain sized dyeings which equal corresponding unsized dyeings in tinctorial strength.

In the following table are recorded the percentage color precipitation of several basic dyes under a variety of conditions (in the absence of stock). The amounts of dye, size and alum employed were such as to duplicate the conditions of a 6-pound beater dyeing with 20 pounds of size and 25 pounds of alum. The amount of soda ash employed with Methylene Blue corresponded to 10 pounds in the beater, whereas with the other dyes it

[4] Color Trade J. (1923), **13**, 9.

corresponded to 5 pounds. The residual dye in the filtered solutions was determined by titration with titanous chloride.

TABLE IV
Percentage Precipitation of Basic Dyes

Method	Methyl Violet NE	Methylene Blue	Victoria Green SC
Dye + soda ash	26.8	15.3	58.1
Dye + size	74.8	33.3	55.4
Dye + size + alum	78.0	33.3	48.0
Dye + alum + size	37.8	5.3	20.3
Dye + soda ash + size + alum	80.3	28.7	83.8

The results obtained illustrate the extreme variation in behavior between individual basic dyes. The precipitates obtained with soda ash were dye bases, those obtained with size were dye resinates and those obtained with soda ash in conjunction with sizing materials contained both dye bases and resinates. From the tests in which the order of addition of size and alum were reversed it is apparent that whereas the preliminary addition of alum inhibits the precipitation of the dye resinates in a considerable measure, its addition subsequent to that of the size has little effect upon the resinates already precipitated.

In the following table are summarized the results obtained in practical dye tests with the same dyes upon bleached sulphite stock. The conditions employed were those of 6-pound beater dyeings (1,000 pounds of stock) with 6, 20 and 25 pounds, respectively, of soda ash, size and alum. The rating of the dyeing methods was made on the basis of comparison of the tinctorial strength of the paper sheets obtained.

TABLE V
Basic Dyes on Bleached Sulphite Stock

Number and Method	Methyl Violet NE	Methyl-lene Blue	Victoria Green SC	Aver. Rank
1. Dye + soda ash + size + alum	1	5	1	1
2. Dye	3	1	5	2
3. Dye + size	7	3	4	3
4. Dye + soda ash	4	2	8	3
5. Dye + size + alum + soda ash	5	8	2	4
6. Dye + size + alum	6	10	3	5
7. Dye + size + soda ash	2	6	11	5
8. Dye + alum + size + soda ash	8	7	7	6
9. Dye + soda ash + size	9	4	10	7
10. Dye + soda ash + alum + size	10	9	6	8
11. Dye + alum + size	11	11	9	9
12. Dye + alum	12	12	12	10

It will be evident that Methods Nos. 2, 3, 4, 7, 9 and 12 do not provide for the sizing of the paper and are included merely to render the data more complete.

The best average results were obtained, as with acid dyes, by "the soda ash treatment" (Method No. 1). In each instance this proved decidedly more effective than Method No. 6, which may probably be accepted as fairly representative of general beater usage. On the other hand, the latter method proved decidedly more effective than Method No. 11, which is essentially similar to the practice advocated by Sunderland.[5] Similar results were obtained in less comprehensive tests with other basic dyes, although minor variations in behavior were noted.

The comparative results obtained with Methods Nos. 6 and 11 and with Methods 1 and 10 afford evidence of the important influence of the order of addition of sizing materials in dyeing bleached stock with basic dyes. The addition of the size should unquestionably precede that of the alum.

In the customary dyeing practice with basic dyes and bleached stock the coloring agent is the dye resinate. A portion of this is formed in the dye liquor with the addition of the size and retained mechanically in the sheet together with the resin and resinate of alumina which affect the sizing. A second portion is probably formed directly upon the surface of the stock by reaction with dye already adsorbed and present in the form of a surface deposit of dye base.

With the soda ash treatment the color deposit contains considerable dye base as well as dye resinate, as is indicated by the fact that the shades obtained are intermediate between those of sized and unsized dyeings in the usual practice. The precipitation of dye bases in the dye liquor is assumed to involve detrimental effects by Kress[6], but that assumption is not necessarily valid. With eleven out of twelve basic dyes which were thoroughly investigated in laboratory dyeings the results obtained were excellent in all respects. In the individual instance of Crystal Violet it was found, however, that although the soda ash treatment resulted in an appreciable improvement in dye strength the dyed sheets were not free from minute color specks.

The Soda Ash Treatment with Basic Dyes

With 20 pounds of size and 25 pounds of alum it was found advisable to employ 10 pounds of soda ash in the instance of Methylene Blue and 5 pounds with Victoria Green, Methyl Violet and Auramine. The results obtained were greatly influenced, as has been shown, by the order of addition of the materials. Optimum results were obtained by adding the soda ash after the dye and before the size and deferring the addition of the alum until the conclusion of the dyeing.

The general improvement in dye strength was considerable with bleached sulphite and rag stocks. With bleached soda pulp, on the other hand, it was only slight. It is of interest to note that a moderate but distinct improvement was obtained with ground wood, although the actual percentage color retention was no greater than in dyeings by the usual method. It appears probable that in the usual practice of dyeing ground wood with basic dyes a portion of the color is deposited within the fiber substance where it is obscured by the capacity of the material.

The degree of improvement on bleached sulphite and

[5] Paper, April 4, 1917.
[6] Paper, Jan. 7, 1920.

rag stocks was particularly decided with Methylene Blue and Victoria Green, but was considerable with all dyes tested. The gain in dye strength was proportionally greater as the amounts of dye employed were decreased.

The shades obtained differed somewhat from the usual shades. The dyeings were somewhat brighter and more attractive than dyeings obtained in the usual practice and proved slightly faster to light. With one single exception of Crystal Violet, already noted, the uniformity of coloring was excellent.

Conclusions

Ample experimental evidence has been obtained of the utility of the employment of soda ash in the beater in effecting improvement in the coloring of sized papers of a variety of materials with both basic and acid dyes. The practice advocated by Mann does not involve modification of the beater acidity of customary practice, but it is believed by the writer that appreciable reductions in beater acidity will usually be required in order to obtain optimum results in respect to tinctorial strength.

The experimental dyeings which have been summarized were carried out, for the greater part, in large cups, provided with stirrers, in which stock was colored which had been previously beaten in laboratory beaters. In some instances the results were confirmed by beater dyeings in the laboratory. Distilled water was employed in all tests. It will be obvious that optimum conditions in operations upon a mill scale will probably differ in some degree from those established in the laboratory, and that it will be necessary, in particular, to provide suitable compensation for the hardness of the water supply at the mill. The formulae employed in the laboratory, accordingly, are not recommended for general mill application. It is only the general principle of the treatment, as outlined, which is advocated.

It may possibly be found that the addition of sufficient soda ash to insure maximum color retention may entail detrimental consequences in other respects. Some degree of interference with the satisfactory sizing of the sheet may possibly result, although no effects of that nature have been observed in any of the experimental dyeings. Some increase in foaming may probably be anticipated. It is believed, however, that with the great majority of dyes and stocks it will be found possible to employ sufficient soda ash to obtain optimum results without serious consequences in any respect.

Practical Hints on the Production of Bright Colors on Textile Fabrics

Part VI

Ordinary Dyeing Machine—Its Operation—Another Type of Machine—Dyeing with Weak Baths —Operating the Plant—Its Advantages

By RAFFAELE SANSONE

Ordinary Dyeing Machine

An ordinary type of dyeing machine for a series of chains of cotton cloth is constructed on the principle shown in Fig. 9.

This shows a long, heavy wooden vat (V) having at the end a double iron frame or arm (B) which collects the series of warps from several distribution cones (Z) and delivers them to a special guide (G) which keeps them a short distance apart.

From here the material makes its way into the dye bath, kept at the required temperature by a long, closed copper coil, and passes over a number of lower and upper guiding rollers before entering between the first pair of squeeze rollers (U). These press out all excess of bath, delivering the series of chains of cloth first to a guide and then to another lot of lower and upper guiding rollers; at the end of them is a second pair of squeeze cylinders (T).

These are followed by other guiding rollers and a final pair of squeeze cylinders (S), which are kept under a stronger pressure than in the case of the other two (T and U). Cylinders S are followed by an exit frame A with a distribution roller on the end of it (R), from which the series of chains form independent cones or balls. On leaving the machine the cloth can be dried or subjected to rinsing on a second machine, in accordance with the intensity of shade dyed and the nature of the dyestuff sand chemical used. The output is usually large. The circulation of the dye bath is conducted from a cistern placed in a higher position at the back of the plant.

Another Type of Machine

Another type of dyeing machine which could also be used for dyeing bright colors with direct coloring matters is constructed on the principle outlined in Fig. 10.

This shows a heavy iron tank (V) of special shape, the interior of which is copper-plated. This vat or trough is mounted on a solid iron base set into the floor of the dyehouse. To its upper portion is fitted a strong iron frame supporting the end shafts of a large roller B below a much smaller roller C which serves to carry the

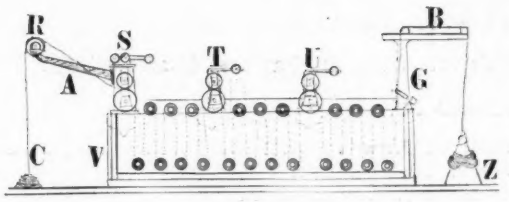


Fig. 9

chains of cotton cloth (M). This cloth passes several times through the dye bath in V, being kept in a slack condition and making its exit on the beater roller D, which is turned by a small pulley (J) fixed to one of the end shafts of bowl B by the leather belt L. Roller D is sustained by a projecting arm A. The dye bath used for the treatment of the goods is introduced in this instance from an upper vat by a large tube (P) and a tap (T).

Dyeing with Weak Baths

A majority of the processes at present used for the dyeing of cotton cloth chains are based on the employment of baths using large quantities of dyestuff, and generally a good portion of this is lost, especially when the color is changed; often the old baths cannot be utilized for following dyeing operations.

The high cost of dyestuffs sometimes makes it imperative to adopt economical methods—the use of weak baths or those not using precipitants, such as salt or sulphate of soda. For this purpose we shall consider a plant constructed on the principle indicated in Fig. 11.

This shows a high iron cover (H) fitted at a certain height below the roof of a dyeing shed and having a number of guiding rollers. Here the chains of cotton cloth are submitted, in a uniformly separated condition, to four different treatments in the spaces indicated by M, N, O and Q; that is, to dyeing and drying, drying without wetting, dyeing and drying, and a final drying.

For the dyeing and drying operations the chains of cloth (E) enter the two apparatus S and T, the lower portion of which contains the dyeing vats V and U. These have a special guide (L and K in each case) containing several guiding rollers running across the vat. The different chains (E) passed through the machine remain each time in their allotted position. They are

(*Continued on page* 571)

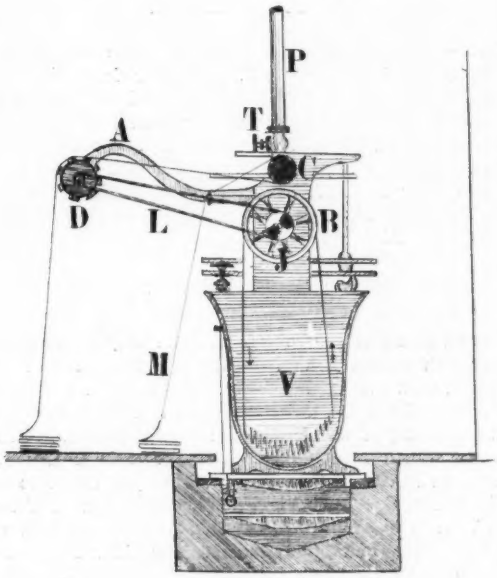


Fig. 10

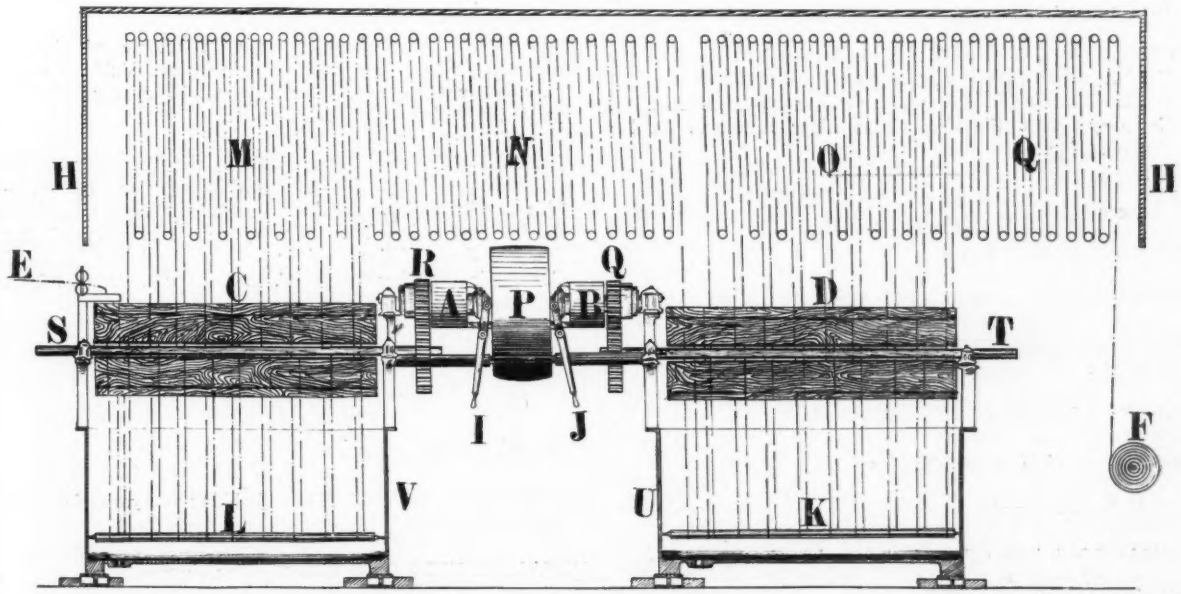


Fig. 11

Dyestuff Tables

A List of the Principal American-Made Colors with Their Properties and Fastness Characteristics

[NOTE: The publishers of The REPORTER have secured more or less complete data in regard to many of the dyestuffs which are at the present time being manufactured in the United States. As the following material has been brought togetner from various sources, they realize that errors are quite likely to appear, and it is earnestly requested that any readers who find errors or who are able to give additional information will communicate with the publishers in order that this material may be made as correct, complete and up to date as possible. These tables will appear serially until all colors upon which we have data shall have been covered. The publication of this data was begun in the issue of March 10, 1924.]

[Note.—The publishers find that the name of the Palatine Aniline & Chemical Corp. (F. E. Atteaux & Co., selling agents) has been omitted under "Competing Products" in many instances where the name should have appeared. They are therefore glad to print the following list of Schultz numbers of the colors manufactured by this firm which have appeared in these tables to date: 9, 11, 15, 19, 29, 33, 34, 37, 38, 39, 40, 41, 42, 48, 56, 57, 58, 61, 65, 66, 67, 70, 79, 82, 89, 91, 94, 102, 112, 114, 133, 145, 154, 155, 156, 160, 161, 163, 168, 171.]

LITHOL RED R

(Schultz No. 173)

This is an insoluble azo color which can only be dissolved in water with great difficulty. To form the lake the color paste is boiled with the substrate with an addition of barium chloride. The shade is a fine bluish red and when mixed with white covering colors the bluish tone still remains. The fastness to light is moderate, much less than Lake Red P. It shows good fastness to water, but is very sensitive to acids. It is fast against carbonic acid, however, but sensitive to alkali. It is insoluble in oil and somewhat soluble in wood alcohol. The product is well adapted for the manufacture of oil colors and for book printing and lithographic printing inks, but is not well adapted for lime and wall-paper colors, as in contact with lime the color becomes dull and has not the covering power.

COMPETING PRODUCTS: Made in the United States by California Ink Company; Cincinnati Chemical Works; Dye & Chemical Manufacturing Corporation; Po Ambo Chemical Company; Ultro Chemical Corporation; American Aniline Products, Inc.

MORDANT YELLOW

(Schultz No. 177)

COMPOSITION: Mono azo.

SPECIALLY SUITABLE FOR: Wool.

USUAL METHOD OF DYEING: Top or bottom chrome or chromate.

SHADE: Slightly redder than S-48.

SHADE BY GASLIGHT: Redder.

SOLUBILITY: Good.

LEVEL: Much better than S-48, especially in light shades.

EXHAUSTS: Very slowly.

FASTNESS TO:

Acid: Redder with mineral acids; O. K. with organic acids.
Alkali: Slightly redder.
Carbonizing: Changes shade.
Cross-Dyeing: Not suitable.
Fulling: Bleeds very slightly in strong fulling, and tints white wool.
Ironing: Fast.
Light: Inferior to S-48 in this respect.
Perspiration: Fast.
Potting. Fast.
Rubbing: Fast.
Scouring: Bleeds slightly; top-chromed dyeings are best.
Steaming: Excellent fastness.
Sulphur: Shade goes duller and greener.
Washing: Bleeds slightly; top-chromed dyeings are the fastest.

SENSITIVE TO METALS, LIME: Sensitive to copper and iron.

MACHINE DYEING: Suitable.

OTHER PROPERTIES: Used in combination mode shade with Chromate Brown EB, Alizarine Blue Black B and Alizarine Red W.

DYED BY OTHER METHODS: May be dyed by the oxalic fluoride of chrome method and used to shade the Anthracene Blues. Silk-white process leaves the silk-effect threads white, but the color does not exhaust well with acetic acid. Dyed chromate, shade is weaker; silk-effect threads are left white. Dyed top chrome on wool, cotton-effect threads are left white.

ON OTHER MATERIALS: Silk: Mordanted with chloride of chrome, the color is fairly fast to water and soaping on this fiber.

PRINTING. Printed on cotton with acetate of chrome. Adapted for printing on wool pieces and slubbing on a chrome mordant. The color may also be dyed on chrome padded and discharged cotton pieces.

COMPETING PRODUCTS: Made in the United States by Amalgamated Dyestuff & Chemical Company; American Aniline Products, Inc.; Cincinnati Chemical Works; National Aniline & Chemical Company; New England Aniline Works; Grasselli Dyestuff Corporation; Palatine Aniline & Chemical Corporation (Selling Agents, F. E. Atteaux & Co.); E. I. du Pont de Nemours & Co.

ERIO CHROME BLACK T

(Schultz No. 183)

COMPOSITION: Mono azo.

SPECIALLY SUITABLE FOR: Slubbing and yarns for worsted goods.

USUAL METHOD OF DYEING: Top chrome.

SHADE: Jet black.

SHADE BY GASLIGHT: No change in shade.

SOLUBILITY: Excellent.

LEVEL: Excellent as a black.

EXHAUSTS: Not clear.

PENETRATION: Excellent.

FASTNESS TO:
Acid: Fast.
Alkali: Fast.
Carbonizing: Fast.
Fulling: Fast to severe fulling; does not bleed into white.
Ironing: Fast.
Light: Very fast; O. K. for men's wear.
Perspiration: Fast.
Potting: Excellent fastness; can be used in fancies against white worsted cotton or silk.
Rubbing: Fast.
Scouring: Very fast.
Steaming: Very fast.
Sulphur: Very fast.
Washing: Very fast.
Water: Stands Markischer test.

SENSITIVE TO METALS, LIME: Sensitive to iron and copper.

MACHINE DYEING: Suitable.

PRINTING: One of the best blacks for vigoureux printing.

COMPETING PRODUCTS: Made in the United States by American Aniline Products, Inc.; Butterworth-Judson Corporation; Cincinnati Chemical Works; E. I. du Pont de Nemours & Co.; United States Color & Chemical Company.

ERIO CHROME BLACK A
(Schultz No. 184)

COMPOSITION: Mono azo.

SPECIALLY SUITABLE FOR: Wool.

USUAL METHOD OF DYEING: Top chrome and chromate.

SHADE: Jet Black; redder than S-180 and S-181.

SHADE BY GASLIGHT: Redder.

SOLUBILITY: Excellent.

LEVEL: Very good.

EXHAUSTS: Almost clear.

FASTNESS TO:
Acid: Fast.
Alkali: Fast.
Carbonizing: Fast.
Cross-Dyeing: Not as fast as S-180.
Fulling: Fast.
Light: Fast enough for men's wear.
Perspiration: Fast.
Potting: Not as fast as Erio Chrome Black B or T.
Rubbing: Fast top chrome; not fast chrome mordant.
Scouring: Fast.
Steaming: Fast; shade goes trifle greener.
Sulphur: Fast.
Washing: Fast.

SENSITIVE TO METALS, LIME: Sensitive to copper and iron.

DYED BY OTHER METHODS: Can be dyed chromate in light percentage only, giving silver-tone grays.

ON OTHER MATERIALS: No interest.

PRINTING: Suitable for vigoureux printing, but the T is better. The printed shade is fast to steaming, scouring and fulling.

COMPETING PRODUCTS: Made in the United States by American Aniline Products, Inc.; Butterworth-Judson Corporation; Cincinnati Chemical Works; E. I. du Pont de Nemours & Co.; Grasselli Dyestuff Corporation; National Aniline & Chemical Company; United States Color & Chemical Company.

LANACYL VIOLET B
(Schultz No. 186)

COMPOSITION: Mono azo.

SPECIALLY SUITABLE FOR: Wool.

USUAL METHOD OF DYEING: With ammonium acetate below the boil.

SHADE: Bluish violet.

SHADE BY GASLIGHT: Very much redder.

SOLUBILITY: Good.

LEVEL: With care, dyes about the same as the Sulphon Acid Blues (S-188 and S-189).

EXHAUSTS: Does not exhaust well.

FASTNESS TO:
Acid: Moderate.
Alkali: Moderate.
Carbonizing: Shade returns on neutralizing.
Cross-Dyeing: Not suitable.
Fulling: Moderate.
Light: Good fastness to light.
Perspiration: Fast.
Rubbing: Fast.
Steaming: Fairly fast.
Sulphur: Moderate.

SENSITIVE TO METALS, LIME: Sensitive to chrome; the shade is much duller.

OTHER PROPERTIES: The shade is dulled by boiling, as the color is somewhat decomposed at the boil.

DYED BY OTHER METHODS: Can be dyed on a chrome mordant; shade is duller, but faster to washing and fulling.

ON UNIONS: Cotton-effect threads are left white. White silk-effect threads are stained.

COMPETING PRODUCTS: Made in the United States by E. I. du Pont de Nemours & Co.

(*Continued on page* 573)

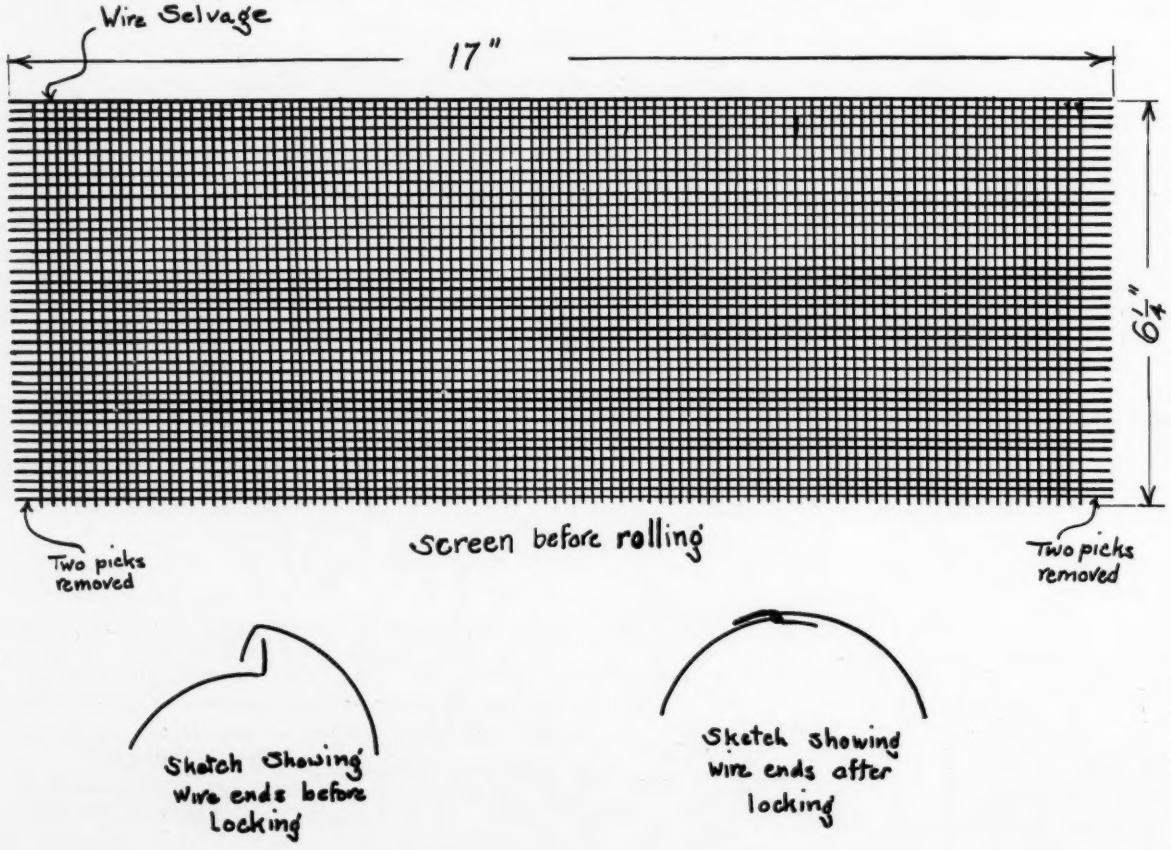
The One-Pound Franklin as a Raw-Stock Machine

By JOHN H. HOLTON, Chem. Eng.

MANY dye laboratories are now equipped with the one-pound Franklin package dyeing machine, which gives excellent results for all package dyeing experimental work and may even be adapted to beam dyeing work by the use of a correction factor to care for the difference in volume ratio. But many such laboratories find themselves without a suitable raw-stock dyeing machine. This handicap means that all experimental raw-stock dyeing must be made either in the laboratory dye pot or on the full-scale plant machine. While the former method is often satisfactory for the matching of shades and the determination of the dyestuff formula, it does not give the important information as to the even dyeing or complete oxidation obtained when dyeing in a circulation machine for raw stock, such as the Vacuum or Chattanooga type. This is of particular importance when using sulphur blues or vat colors.

In order to obtain this desired information those laboratories possessing a one-pound Franklin machine may easily convert this into a very satisfactory raw stock machine. A piece of heavy galvanized screen, such as is used in a cotton condenser, is cut into a rectangle 17 inches long by 6¼ inches wide, with the wire selvage on the long side if possible. The two short ends are unraveled for about two picks. Then the sheet is rolled into a cylinder and the wire ends bent over as a lock. These may be touched with a drop of solder, although when properly locked no solder is required and there is no interference with the circulation of the dye liquor. No bottom to the cylinder is required, for when one is used there is a loss in pressure on circulation due to a short circuit of the liquor under the bottom of the screen.

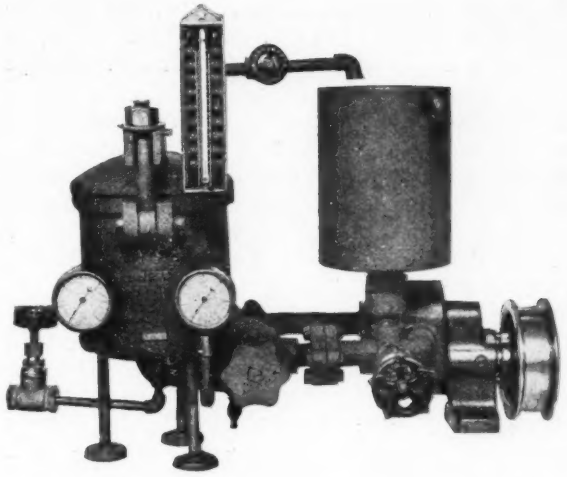
When charging the machine with raw stock the cylinder is placed in the kier and centered. The kier is then half filled with water and the cotton is packed down into the annular space around the core, care being observed to maintain the proper centering of the screen. Lugs may be fastened to the screen to keep it centered if desired. Careful and tight packing is essential to even circulation, as in any raw-stock circulating machine. The machine when filled should hold from 250 to 350 grams of cotton. The regular



clamp used for the packages is then forced down on top of the cotton. Care should be observed that there is sufficient cotton to cover well above the top hole in the core. It has been found that for laboratory purposes a better clamping of the packages and the cotton can be obtained when the regular notched core furnished with the machine is replaced by one with a threaded top and a large thumb screw provided to give any desired compression to the charge.

In dyeing the raw stock any desired method of operation may be employed, it, of course, being advisable to duplicate as nearly as possible that used with the full-scale machine. As most raw-stock machines provide for circulation in but one direction this machine will probably be operated with the circulation all one way.

With such an installation it will be found that the best operating conditions for even dyeing and complete oxidation of raw stock may be more easily studied. It will, of course, be necessary to establish conversion factors so that the dyestuff formula on the small machine will give the exact shade on the larger machine, where the volume ratio may be quite different. However, with a little practice this equipment will be found to be of considerable value to the chemist and dyer.



Treatment of Waste Waters From Dyeing Processes*

Arsenates and Phosphates—Recovery of Alizarine—Recovery of Tin from Waste Waters—Recovery of —Screening—Settling—Recovery of Indigo Waste—Treatment of Sulphide Dye Waste

By S. N. BROWN

ALTHOUGH the actual waste in dyehouse effluents is not great, owing to the efficient methods now in vogue, there is still a considerable amount of valuable products discharged into the streams and sewers. Such waters may contain, among other matter, valuable salts from mordanting and wash baths, soap, grease, textile fibers, etc., according to the various processes conducted at the works. No large profits can be made by the recovery of these products, but a considerable economy may be made thereby when treating the effluent to render it suitable for discharging into streams.

Recovery of Tin from Waste Waters.—Stannous and stannic salts are important mordants, and are also used for weighting silk. Practically 50 per cent of the tin is lost in the mordant and dye baths, and in the wash waters.

A method for the recovery of the tin has been given by M. Moyret (Mon. de la Teinture, 1889). The waste liquors are collected in tanks, and the tin is precipitated by the addition of zinc dust or granulated zinc. The precipitate, which consists of metallic tin and stannic oxide, is filtered through woolen cloth, washed, dried, and melted at a white heat, with the addition of borax and a little granulated zinc. The stannic oxide present is reduced to metal by the zinc, excess of zinc being volatilized at the high temperature employed. Pure metallic tin is thus obtained.

Recovery of Arsenates and Phosphates.—A process for the recovery and subsequent utilization of arsenates and phosphates from the "dunging" process or fixation of the mordants, has been patented by Higgins and Stenhouse. Their method consists in mixing the waste liquors with an iron or manganese salt, making the mixture alkaline with milk of lime and allowing to settle. The top liquor is decanted and the precipitate is placed on cloth strainers. A quantity of sodium sulphide proportional to the bases present is added, and the mixture boiled with water in a steam jacketed pan for two hours. A clear solution is obtained which contains sodium arsenite, sodium arsenate and sodium phosphate. Excess of sodium sulphide is oxidized with sodium hypochlorite, and the excess of alkalinity is removed by addition of mineral acid. The solution can then be used as in the original process.

Recovery of Alizarine from Waste Liquors.—In the dyeing of Turkey Reds and other shades, in which alizarine is used, a certain loss of dye is entailed. Remners has patented the following method of recovery: In a large tank fitted with stirirng gear, sufficient hydrochloric or sulphuric acid is added to the waste liquors to precipitate the whole of the coloring matter. The liquor is allowed to settle and the clear, upper layer of liquid drawn off.

*From the Journal of the Society of Dyers and Colourists.

The precipitate is boiled for a few minutes until the liquor becomes yellow in color. After cooling, the precipitate is filter-pressed and washed till neutral. The dye obtained can then be used again.

Although effluents vary considerably in different works, they can always be subjected to similar treatment, i.e., screening and settling, with or without chemical precipitation, followed by filtration, in order to produce an effluent suitable for discharge into sewers, etc. Suitable screening should first be adopted in order to prevent the escape of loose fibers, which occurs chiefly in woolen mills. These fibers represent a considerable market value which amply repays the cost of the screening apparatus. If they are not removed they also add greatly to the amount of sludge obtained and increase the difficulties of purification, e.g., by forming a felted layer on the filter beds.

There are a number of methods in use for the further treatment of the waste waters depending on the mode of adding the precipitant, kind of settling tank employed and form of filter used.

Screening

There are various arrangements for the removal of loose fibers from effluents, such as the Kent's screen, Chambers & Hammond screen, etc., in which the fibers are mechanically removed from the effluent. One of the simplest contrivances consists of a box, the bottom of which is made of perforated copper, on which the fibers are retained, while the waste liquor runs through. It is not efficient, however, as in many cases 25 per cent of the total fiber passes through the perforations.

Settling.—A simple method consists in having a number of tanks fitted with sludge filters. Seven such tanks, having a capacity of 56,000 gallons, were used in treating a dyeworks effluent of 40,000 gallons per day. This effluent was produced in the dyeing and finishing of cotton cords, and contained from 10 to 20 parts per 100,000 of suspended matter. By settlement in the tanks, this was reduced to three parts per 100,000. At certain intervals the tanks were run off to the sludge filters and the resulting sludge allowed to dry. By this method eight tons per annum of dried sludge were removed from the works.

A number of patented apparatus are in use, generally on the principle of water-softening plants, i.e., the necessary amount of precipitant chemicals, usually milk of lime, soda, and alumina-ferric, are added to the effluent, and the precipitate filtered off.

Recovery of Indigo Waste

From Indigo waste waters most of the residual dyestuff can be obtained by suitable treatment.

In the old methods of dyeing, using the fermentation vat, the accumulated sludge at the bottom of the vat was thrown on the waste heap and the waste liquor allowed to drain off. This represented a considerable loss of valuable dye. A loss of Indigo also occurs during washing after dyeing. In some cases over 8 per cent of the total Indigo used was lost in washing.

The liquid refuse from the process of Indigo dyeing consists of the contents of the vats when they are discharged and of the daily discharge of wash waters. Not only do they contain waste Indigo, but they are often too polluted to be discharged into streams.

Much loss of Indigo also occurs during the dyeing of loose wool. When taken out of the vat a certain amount of loose Indigo clings to the wool. A portion of this is washed off with acidulated water, but a large proportion remains in the after processes of carding, spinning and weaving. The loose Indigo is finally removed during soap scouring. If the soap liquors are acidified for recovery of grease, the Indigo is left behind in the residual pressed cake, after removal of the grease.

The recovery of this waste Indigo has been carried out successfully by several large works in Lancashire and Yorkshire. For a works using a large amount of Indigo the recovery is exceedingly remunerative.

Before the war a certain large dyeworks used about $23,400 worth of synthetic Indigo per annum. Out of this $7,000 worth of waste Indigo was recovered from the solid which settled at the bottom of the dye vats and from the wash waters.

The wash waters are first precipitated in tanks under the floor of the works with Alumina-ferric and caustic soda; the top water is drawn off by means of a valve with a floating arm, and the solids, together with those from the dye vats, are pumped up into a tank where they are treated chemically for the recovery of the Indigo, which is used again in the dyehouse.

The waste Indigo from wool dyeing is chiefly found, as previously stated, in the pressed magma cake resulting from grease extraction. It has been suggested that after degreasing, the cake should be vatted or reduced and the Indigo dissolved and recovered afterwards by oxidation. If the spent contents of the Indigo vats are not recovered (this applies also to the first washings of the dyed goods), then the Indigo present settles out with the sediment formed in the general refuse of the works. Such a mixed sludge may contain from 1 to 6 per cent of Indigo.

From an economical standpoint, it is inadvisable to recover the Indigo from such a mixed sludge. On the other hand, it would be possible to recover the Indigo from the vats and first washings, before mixing with the general effluent.

Treatment of Sulphide Dye Waste.—Although most of the dye vats are not directly discharged on dyeing a batch of goods, but are used for the preliminary treatment of a fresh batch of grays, etc., the ultimate discharge from these vats, consisting as they do of a considerable amount of sulphides, are a grave sort of inconvenience when they come in contact with any acid water, giving off quantities of sulphureted hydrogen. As in the case of the treatment of kier liquors from a bleach croft, these sulphide liquors must be treated separately before discharging into the general waste tanks. Mackey's method consists in collecting the waste waters in a settling tank and precipitating the sulphides and organic matter with a suitable mixture of lime and copperas, the contents being agitated by

means of air blown in by a steam injector. The precipitate is allowed to settle for several hours, and the clear upper layer discharged through a floating valve to the sewer. The sludge is let off frequently and filtered, and allowed to dry. Although the effluent produced by this treatment is fit for discharging into the sewers, it would require further treatment before passing into a stream.

Chambers & Hammond have designed a plant capable of treating such waters to make them suitable for discharging into streams. The process depends on the principle of aerating the liquors in order to oxidize any offensive sulphureted hydrogen and then precipitating the sulphides and organic matter with alumina-ferric, the sediment being collected in tanks of an inverted pyramid shape, the final liquor being filtered through fine wood shavings. By this method most of the sediment is removed.

PRACTICAL HINTS ON THE PRODUCTION OF BRIGHT COLORS ON TEXTILE FABRICS

(*Continued from page 565*)

passed through wooden separators (C and D) having pot holes. In order to dye the series of chains of cotton cloth at different speeds, the driving pulley P, working every portion of the plant, is regulated in its action by lever J, collar B, the pinion wheels Q and another special mechanism not seen in the figure. The plant can be stopped or worked by moving the lever I before the collar A and pinion wheels R. At the end of the plant is a special winding mechanism (F), by which each warp of cloth is wound on its own layers without being submitted to any turning or twisting.

The plant receives the warps of cotton cloth from a shaft which in turn has received them from a machine where they have been brought in this form from the full width, without twisting them in any way, and by the arrangement of all guiding rollers under cover H no folding follows during the dyeing.

Operation of the Plant

To work the above plant the operators enter thin cotton tapes on all guiding rollers in the dye vats L and K and below cover H, preventing any turning of the tapes and causing them to pass between the guides C and D. When the tapes have been properly placed, the operators enter steam in radiators below cover H to work the plant and the mechanism J, B, Q, which makes it possible to dye the material quickly, a desirable feature when light shades are to be produced. This is done after the weak dye bath has flowed slowly through the lower portion of vats L and K, so that it just covers the material.

The cloth passing through the machine is thus repeatedly washed in vat L and repeatedly dried below cover H. It is allowed to remain moist enough to assure a better penetration of the dyestuff solution, which deposits layer after layer of color on the material. The cloth, of course, receives some degree of shade when it passes through the portion indicated by N, where a drying operation is conducted before the material passes into the second dyeing apparatus T. Here a repetition of the first wetting and drying operations takes place, followed, in the portion indicated by Q, by the last drying operations.

Advantages of the Plant

This plant has the following advantages:

1. The material can be dyed with one or two colors.
2. The speed of the machine can be regulated to produce, from one weak dye bath, light, medium and dark shades, greatly simplifying the weighing operations.
3. The cost of the dyeing operations is small, as the machine uses little dyestuff and requires only moderate labor and motive power.
4. A poor shade observed after the exit from apparatus S can be often corrected on apparatus T.
5. If required, vat K can be used for soaping, chroming or coppering operations, reducing the strength of the bath and greatly increasing its volume.
6. The spreading of the ropes of cotton cloth can be accomplished without any untwisting and on a very simple apparatus, requiring less time than is usually necessary.
7. The dye baths used being weak, the waste of coloring matter is low.

(*To be continued.*)

A KNITTER'S COUNTING BOARD

In the July 28th issue of The Reporter there appeared, in an installment of the Journal of a Hosiery Dyer, an item headed "Shortages" in which the dyer told of complaints from the mill regarding shortages in dyed lots of hosiery. The dyer proceeded to explain how the knitters, who work on piece work, had passed through and labeled as a dozen pairs bundles containing only eighteen or twenty stockings. In connection with this practice there is a remedy on the market in the form of a device known as a knitters' counting board, consisting of a board with 24 pegs on which the hose are hung by means of the open toe as they press off the machine. When all the pegs are covered the operator has one dozen pairs and can bundle the hose without counting them. Anyone interested in securing further information regarding this simple yet extremely useful counting board may communicate with the American Dyestuff Reporter.

The existence of the Essen Sales Association for Tar Products (Verkaufsvereinigung fur Teererzeugnisse in Essen) has been automatically prolonged until the end of 1925. Various new internal arrangements have been made between the members of the Benzolvrband, the most important of which is the formation of a joint selling agency for benzol between the Rhenish steel works and the Koln-Neuessener Bergerksverein.

Technical Notes from Foreign Sources

Effect of Sulphuric Acid on Breaking Load of Cotton

A study has been made of the effect of sulphuric acid solutions on single cotton fibers and on cotton yarns as well. The investigation was made by means of breaking load tests on a modified form of the O'Neill apparatus or a Baer single thread tester.

The samples were first soaked in the acid for a period of two days at the ordinary atmospheric temperature. Then they were thoroughly washed and dried in the air. It was found that when the samples of cotton were treated with a 10 per cent solution of sulphuric acid, distinct tendering of the fibers was produced. Complete destruction of the fibers was caused by an acid containing 77 grams of sulphuric acid per 100 c.c.

It was also established that in the case of single fibers, the tendering effect is directly proportional to the concentration of the acid. In the case of yarns, the strength decreases slowly, but in proportion to the concentration of the acid until this concentration reaches a point between 20 to 30 per cent. Thereafter, the concentration of the acid falls more rapidly, but the proportional relationship still exists.

The structure of the yarn seems to have an important effect on the results obtained in testing them. During the first period, the yarn breaks mainly by slipping, but in the second period the individual fibers are already so weakened that they snap without slipping. Examination of the fibers under the microscope shows the difference between the slip break and the snap break. When greater concentrations of acid are employed, the fibers are so strongly affected that a white dust shakes off when they are handled immediately after drying.

The conclusion must be reached that although kier boiling weakens the single fiber, nevertheless it strengthens the raw yarns or the yarns that have been treated with sulphuric acid of concentration lower than 10 per cent. This is due to the closer packing of the fibers in the yarns, which prevents slipping.

Further details are to be found in the original article in the Journal of the Textile Institute, 1924, pages 281, 290T.

Printing Animal Fibers with Vat Dyes

The addition of ammonia, ammonium carbonate, or ammonium bicarbonate, or mixtures of these, to vat dyestuffs for printing animal fibers, prevents injury to the fibers during the process. The dyestuffs may be reduced previous to printing. German Patent No. 391,995.

Sodium Phosphate in Silk Weighting

An investigation was made for the purpose of determining the effect of sodium phosphate, the role that it plays in the process of weighting silken fabrics by the stannic acid-phosphate process. To do this various experiments were made with dilute solutions of phosphoric acid, sodium dihydrogen phosphate, disodium hydrogen phosphate and trisodium phosphate and their reaction on suspensions of stannic acid.

It was found in the first place that the phosphate and the sodium ions are absorbed independently by stannic acid. The increase of the temperature at which the experiment was carried out results in an increase in the adsorption of phosphate ions from acid solutions (phosphoric acid and sodium dihydrogen phosphate), but it has the opposite effect in alkaline solutions (disodium hydrogen phosphate and sodium phosphate). The adsorption of sodium ions from the different solutions varies but little, but decreases rapidly above 50 deg. Cent. The adsorption of phosphate ions exceeds that of sodium ions except from solutions of trisodium phosphate.

It was also found that a certain amount of stannic acid passes into solution, probably in the colloidal form. The stannic acid, after treatment with disodium phosphate, can be completely dissolved by repeated washing with water, but is insoluble in 1.5 per cent hydrochloric acid.

Further details are to be found in the original article, Helv. Chim. Acta, 1924, 587-604.

Carbonizing Wool

During the process of carbonizing wool, it is essential that the woolen fiber itself be protected as much as possible against the action of the carbonizing chemicals. A German patent (No. 393,728) has been issued in a process of adding certain protective agents which prevent the carbonizing reagents from attacking the woolen fibers themselves. This is done by the addition of various products which are obtained by the decomposition of albuminous substances, such derivatives as lysalbinic and protalbinic acids. Another particular advantage of this process is that in the subsequent combing out of the woolen fibers, there is a smaller proportion of waste than is ordinarily the case.

Dyeing and Printing Silk

French Patent No. 557,106 is concerned with a process for the dyeing and the printing of natural and artificial silk fabrics. The silken fiber, which is degummed in the ordinary manner, is colored with acid

dyestuffs, then washed and dried. Then after mordanting with tannin, drying and treatment with tartar emetic and subsequent drying, the fabrics are printed with basic dyestuffs and then washed. Natural silken fiber is purified by washing with soap.

Effect of Heat on Bleached Cotton Fabric

Bleached cotton yarn was exposed to a temperature of 93 deg. Cent. for 336 hours. After a few days it was seen that the cotton commenced to brown and lose much of its strength. There were indications of the formation of oxycellulose. Yarn which was heated at the same temperature for the same period of time in sealed tubes containing air changed more rapidly, and the whole of the oxygen present was absorbed. Similar slow darkening occurred with other cellulosic materials. This experiment indicates that the temperature of incipient decomposition of cellulosic substances is much lower than assumed. Fuel, 1924, 106.

DYESTUFF TABLES

(*Continued from page 567*)

SULPHON ACID BLUE R

(Schultz No. 188)

COMPOSITION: Mono azo.

SPECIALLY SUITABLE FOR: Wool.

USUAL METHOD OF DYEING: Start dyeing with acetate of ammonia and Glauber salt.

SHADE: Bright reddish blue.

SHADE BY GASLIGHT: Much redder.

SOLUBILITY: About 40 grains per liter.

LEVEL: Moderate; dyes level only with extreme care.

EXHAUSTS: Well with acid.

FASTNESS TO:

Acid: Fast to organic acids.
Alkali: Fast.
Carbonizing: Fast.
Chlorine: Fast.
Cross-Dyeing: Fair; shade is much duller.
Fulling: Moderate; same as S-189.
Light: Very good, top-chromed.
Perspiration: Moderate.
Rubbing: Fast.
Scouring: Moderate; same as S-189.
Steaming: Fast; better when top-chromed.
Sulphur: Not fast; color bleeds.
Washing: Moderate.
Finishing: Not as good as Sulphon Acid Blue B.

SENSITIVE TO METALS, LIME: Not sensitive to copper or iron.

MACHINE DYEING: O. K.

DYED BY OTHER METHODS: Chromate: Dyes more level and leaves silk-effect threads white. Top chrome: The color is faster to steaming and light, but is duller.

ON UNIONS: Suitable for gloria. Cotton and artificial silk-effect threads are unstained in an acid bath.

ON OTHER MATERIALS: Not adapted for cotton-wool unions, as in an acid bath the cotton is not left pure white and in a neutral bath the color does not exhaust well. Silk: Dyes in bath of boiled-off liquor broken with sulphuric acid, but the color is not fast to water on this fiber.

PRINTING: Suitable for printing slubbing (acid).

DISCHARGING: On wool, gives a yellow discharge with tin crystals or zinc dust.

COMPETING PRODUCTS: Made in the United States by Amalgamated Dyestuff & Chemical Company; E. I. du Pont de Nemours & Co.; Grasselli Dyestuff Corporation; National Aniline & Chemical Company; United States Color & Chemical Company.

SULPHON ACID BLUE B

(Schultz No. 189)

COMPOSITION: Mono azo.

SPECIALLY SUITABLE FOR: Wool.

USUAL METHOD OF DYEING: Acetate of ammonia and Glauber salt.

SHADE: Duller and greener than S-188.

SHADE BY GASLIGHT: Duller.

SOLUBILITY: Good.

LEVEL: Moderate; dyes level only with care.

EXHAUSTS: Better than S-188.

FASTNESS TO:

Acid: Fast to organic acids.
Alkali: Fast.
Fulling: Modeate; same as S-188.
Ironing: Fast.
Light: Same as S-188.
Perspiration: Same as S-188.
Rubbing: Fast.
Scouring: Moderate.
Steaming: Fast top-chromed.
Sulphur: Not fast; same as S-188.
Washing: Moderate.
Finishing: Better than Sulphon Acid Blue R.

ON UNIONS: Same as S-188.

ON OTHER MATERIALS: Same as S-188.

PRINTING: Adapted for wool printing with acetic acid.

DISCHARGING: Same as S-188.

COMPETING PRODUCTS: Made in the United States by National Aniline & Chemical Company.

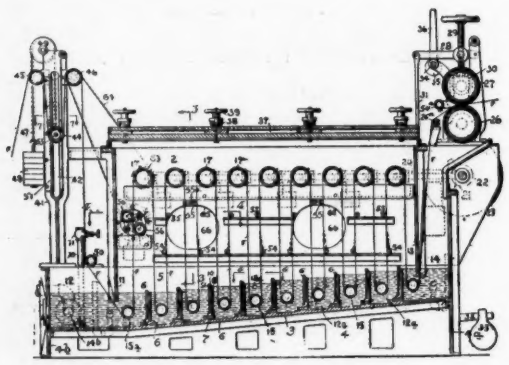
RECENT PATENTS

Machine for Lixiviating Textiles

(1,497,075; June 10)

Charles H. Elliott, Philadelphia, Pa., assignor to H. W. Butterworth & Sons Company, a Corporation of Pennsylvania.

In a machine for lixiviating textile fabric, a chamber adapted to provide a heated atmosphere having its lower part in box-like form divided into a series of transverse trough-like compartments separated by a plurality of transverse walls bolted to the bottom and sides of the box-like structure, the upper ends of said



transverse division walls being successively at higher elevations and each formed by a double transverse wall with a fluid passage between them, said passage opening in one direction at the bottom into the next lower compartment and opening at the top in the opposite direction into the next higher compartment whereby the fluid from the latter compartment overflows the adjacent wall and downward through the passage to the lower part of the next lower compartment and so on through the series of compartments, submerged guide rollers arranged in said compartments, guide rollers arranged in the upper portion of the enclosed chamber whereby fabric is guided alternately around the submerged rollers and upper guide rolls, means for subjecting the fabric intermediate of said rolls to a scouring action, means to admit washing fluid to the uppermost compartment, and a water seal in the lowermost compartment for permitting the entrance of the fabric while maintaining the compartment in a substantially closed condition.

Tetrakisazo Dyes

(1,496,780; June 10)

Werner Lange, Berlin-Friedenau, and Ludwig Neuman, Berlin, Germany, assignors to Actien Gesellschaft fur Anilin Fabrikation, Berlin, Germany.

The herein described tetrakisazo dyes being in the shape of their sodium salts dark powders soluble in water to dark colored solutions not being altered by sodium hydroxide, but from which the dyes are separated by hydrochloric acid, being insoluble in alcohol, ether, benzene being destroyed by strong reducing agents, dyeing cotton gray, to greenish gray tints and corresponding to the general formula: A—azo→M'—azo→M"—azo→M'"—azo→E, in which A, M' and M" are residues of amino compounds of the aromatic series, M'" a residue of an amino-oxnaphthalene sulphonic acid and E the residue of a compound derived from cyclic hydrocarbon.

Manufacture of Vat Dyestuffs

(1,497,231; June 10)

Maximilian P. Schmidt and Alfred Hagenbocker, Biebrich-on-the-Rhine, Germany, assignors to the firm Kalle & Co., Aktiengesellschaft, Bierbrich-on-the-Rhine, Germany.

Process of producing vat-dyestuffs consisting in fusing the condensation product of acenaphthenone and benzaldehyde with alkaline agents.

NEW DU PONT COLORS

E. I. du Pont de Nemours & Co. have placed on the market two new fast pinks for cotton goods. These products we designate as Du Pont Geranine G L and Du Pont Geranine G W.

The "G W" brand will be offered where fastness to washing is of special importance, and the "G L" where fastness to light is of prime interest.

These two new colors in addition to this firm's Pontamine Fast Pink G and "B L" now make it possible to obtain a very full range of shades on cotton goods.

These products have all the usual qualities of good direct dyestuffs. They dye evenly and exhaust well, and can be used on all classes of cotton fabrics.

The Millbank Bleachery, at Lodi, N. J., has awarded a general contract for the erection of a one-story dyehouse addition, 50x170 feet, to cost about $41,000, including equipment.

Frank Lees, chemist for Bosson & Lane, is traveling in England. He is expected to return to America the latter part of September.

YOUNG CHEMIST WANTED

A textile organization in Pennsylvania have a vacancy in their laboratory for a young chemist, preferably one having experience in problems connected with the scouring and dyeing of loose wool and yarns. Good progressive position for the right man. When replying state age, training, experience, and salary expected. Address replies to Box 268, American Dyestuff Reporter.

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Have You a Technical Library?

Every dyehouse and every dye laboratory should have its five-foot shelf of technical books. Where dyes are used day after day those who use them should make it their duty to themselves and to the mill they work for to know something about the theoretical side of dyeing, bleaching, finishing and textile chemistry in general. The value of this knowledge, though it is easily obtainable at very small cost, is usually under-estimated by those who need it most. It is essential in order to be conversant with up-to-date methods and processes that every dyer and textile chemist have ready at hand for convenient reference a row of authoritative technical books.

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